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ERRATUM

Volume 6, *No.* 2, *p.* 170

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read 2.5×10^{-2} NaCl

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GILGAI PHENOMENA IN TROPICAL BLACK CLAYS OF KENYA

I. STEPHEN, E. BELLIS, AND A. MUIR

WITH THREE PLATES

THE investigation reported in this paper arose out of the problem, brought to the notice of the writers in 1952, of uneven growth of crops on several estates in the Athi Plains region of Kenya. This uneven growth occurs as roughly circular 'islands' of 20 to 50 yds. diameter, at 50- to 100-yd. intervals, on which crop growth is very much superior to that in the surrounding areas. The difference is so great in the case of maize (Plate IA), unridged sisal, and abandoned Napier grass, that on the islands vigorous heavy growth is obtainable at a time when in the 'surrounds' the crop will be a failure.

With sorghum and ridged sisal the difference is smaller but still marked (Plate IB), and in an area of heavily grazed *Panicum Makarikariensis* growth differences were so small as not to be noticeable. In natural cover occasional thorn shrubs (*Acacia drepanolobium* and *A. formicarium*) may be found on the islands in areas where no thorn trees are found on the surrounds and most islands carry a dense carpet of star grass when the natural vegetation is of tall-growing tufted grasses. After cultivation *Sphaeranthus bullatus* is frequently conspicuous in the surrounds, but is rare on the islands. During grass fires the vegetation on the islands is markedly less susceptible to burning than on the surrounds.

From the air these contrasting conditions show up very clearly as a honeycomb-like pattern of dots on a contrasting background, and this pattern is well brought out in aerial photographs, an example of which is given in Plate II. The area over which the pattern may be found covers several hundred square miles. The islands supporting good growth are very slightly raised, perhaps 6 in. to 1 ft., above their surrounds. The latter have a reputation for poor drainage, but drainage within the island sites is generally regarded as free.

Among the various suggestions made for the origin of the island sites, termite mounds seemed a possible one, but an examination of the ground has produced no positive evidence that termite activity is responsible. While in many islands ant-bear holes are conspicuous and while part of a termite gallery was found in one of the islands investigated, the opinion of Mr. W. V. Harris, Officer-in-charge, Termite Research Unit at the Commonwealth Institute of Entomology, was that the species concerned was one that would not be expected to build mounds; the gallery was of recent occupation and much newer than the island in which it was found. It appears that termite colonies occupy the islands because of the suitability of the environment there, rather than that the soil conditions in the islands are attributable to past termite activity.

The effect has also been seen by one of us (A.M.) most beautifully displayed in a so-called *mbuga* soil at Ukiriguru in Sukumuland, Tanganyika. In a ploughed field the islands stood out as almost white

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(calcareous) circles of 3 or 4 yds. diameter on an otherwise black soil. In Nyasaland the same observer has noted a similar phenomenon in dambos, but it is less striking unless the grass is burned. The surface of the soil is formed into fairly regular series of low mounds (6 to 18 in. high) with occasional pot-holes, up to 12 to 15 in. deep, in the depressed parts.

The only satisfactory explanation of the phenomenon is that it is an example of what has now generally come to be known as *gilgai* (Hallsworth *et al.*, 1955). What we have termed islands in the above account correspond to the *puff*, and the surrounds to the *shelf* in Hallsworth's nomenclature. The pattern seems to be that of the normal or round gilgai. The pot-hole in the Nyasaland variety would appear to be the sink-hole of Hallsworth *et al.*

The Athi Plains

These lie at elevations of 4,800–5,000 ft. to the east of Nairobi, and are underlain mainly by Nairobi Phonolite which is an intermediate lava of Early Tertiary age. Nairobi Phonolite is characterized by its richness in sodium with the development of such minerals as anorthoclase or soda-orthoclase, nepheline, soda-rich pyroxenes such as aegirine and aegirine-augite, and soda-amphiboles including katophorite and barkevikite. To the west, the Nairobi Phonolite is covered by more recent Trachyte. The Plains are bounded to the east by hills of Basement Complex which contain a wide variety of metamorphic rocks, e.g. mica and mica-hornblende schists and gneisses, kyanite gneiss, sillimanite gneiss, &c.

The rainfall over the Plains averages between 25 and 30 in. a year. Of this, half normally falls in the period March to May, and one-third in the period October to December. The mean temperature ranges from about 61° F. in July, August to 69° F. in February, March. The mean diurnal range of temperature varies from 16° F. in July and in November to 24° F. in February.

Four soil profiles, including specimens of the underlying rock, representative of puff and shelf sites were taken at each of two localities: Embakasi (36° 57′ E., 1° 10′ S.) and Juja (37° 08′ E., 1° 10′ S.).

Petrography of the Underlying Rocks

Embakasi 'shelf site'. The rock is a dark coloured fine-grained lava characterized by numerous clear phenocrysts of anorthoclase, and more rarely of green clinopyroxene and biotite, in an aphanitic groundmass which includes abundant small feldspar laths (probably orthoclase or soda-orthoclase), granules of magnetite, and apatite prisms. The feldspar laths often show a radial arrangement, or in places a marked trachytic texture.

The rock weathers with the development of a greyish crust, thin sections of which show the phenocrystal minerals essentially unaltered, but appreciable amounts of clay material have been developed in the fine-grained base, in places accompanied by calcitization. An X-ray

analysis of the secondary clay shows it to be montmorillonitic in nature, the glycerol-saturated material giving an integral series of 17·7 kX (001) reflections.

Embakasi '*puff site*'. The rock presents similar mineralogical characteristics to the above, but is highly vesicular, and the infillings of the vesicles by secondary products has given rise to a well-developed amygdaloidal structure. The infilling minerals include montmorillonoid, metahalloysite, calcite, opaline silica, and prehnite. In colour the montmorillonoid is variable in shades of light yellowish-brown, and often forms differently coloured zones parallel to the margins of the vesicles. The metahalloysite normally occupies the central core of the amygdales, and occurs as a white granular material of very low birefringence and mean refractive index about 1·55: its X-ray pattern corresponds closely with data given by Mehmel (1935).

Juja '*shelf and puff sites*'. At this locality there is no difference in the rock underlying the two types of site. The rock is pyroclastic in nature, and is a dull greyish rock, which in sections shows numerous clear phenocrysts of anorthoclase and rock fragments in a fine-textured altered brownish matrix, much of which is optically irresolvable. The included rock fragments are often partly rounded, and are of phonolitic or trachytic affinities, one common type showing moss-like growths of aegirine in a largely feldspathic base. Segregations of opaque minerals, green clinopyroxene, apatite prisms, and 'nests' of calcite occur sporadically.

The Soils

The soils of the Athi Plains belong broadly to the Great Soil Group of tropical black earths, the grumasols of Oakes and Thorp (1951), and the margalitic soils of Dames (1949). In this region, however, the soils seem to be generally of no great depth, and at about 36 to 42 in. pass fairly sharply into the undelying weathering lava.

The following profile descriptions are typical:

1. *Puff site:*

0–18 in. Grey, friable, clay loam, with small pockets of pale greyish-brown loam; granular to nutty structure in top few inches, becoming markedly prismatic with depth, carbonate concretions occur; sharp transition.

18–27 in. Greyish-brown, friable clay loam, calcareous with vertical intrusions of surface soil down cracks; carbonate concretions prominent; rounded cavities, some containing recently colonized termite galleries, sometimes occur in lower part of this layer; roots more conspicuous at base; abrupt change.

27–36 in. Carbonate-coated weathering grits with some moderately large stones.

36 in.+ Gradually becoming coarser, the small grits disappearing at about 42 in.

2. *Shelf site:*

0–15 in. Black, columnar-structured, massive, clay; roots frequent near surface, but scarce at depth; fairly sharp change.

15–30 in. Black clay with scattered small calcareous concretions; abrupt change.

30–39 in. Black clay containing pieces of weathering rock.

39 in.+ Weathering rock with black clay along fissures.

The appearance of the shelf profile is typical of large areas of non-calcareous clay mbugas and dambos in Central and East Africa, with their extensive cracking into massive clods during the dry season. These clods are commonly bounded by vertical sides, but the base is often at a decided angle to the horizontal and slickensides on the surfaces become prominent at depth. The differences in structure of the surface layers are well illustrated by the pictures in Plate IIIA and B, although these are from other localities.

The change from the shelf to the puff is fairly sharp, although there is a transition zone in which the massive structure is less well developed. In an example seen in Tanganyika, near Ukiriguru, a layer of carbonate concretions occurring at some depth under the shelf position could be seen in a deep gully section to approach the surface in the puff site. The concretions are presumably gradually squeezed out during the swelling and shrinking of the clay, though the mechanics of the process is as much a puzzle as the formation of the puffs themselves.

Soil Mineralogy

The fine sands (0·2–0·02 mm.) from the soils were examined optically after separation into two fractions with bromoform (S.G. 2·86): the percentage of 'heavy minerals' in the sands is small, being less than 3 per cent. by weight in all the samples. The composition of the light and heavy separates is listed in Table I, the minerals in the first column under each heading being those which have been also noted in the underlying rock samples, or which are known to occur in rocks of this type.

TABLE I

Composition of Fine Sand Separates

Light separate		*Heavy separate*	
Anorthoclase	Quartz	Magnetite	Epidote-clino-zoisite
Lava fragments	Microcline	Aegirine	Zircon
Opaline silica	Albite	Augite or aegirine-augite	Rutile
Calcite	Labradorite	Barkevikite	Green hornblende
	Iron-manganese concretions	Katophorite	Tremolite
	Calcareous concretions	Biotite	Sillimanite
		Apatite	Kyanite
		Sphene	Garnet
			Staurolite
			Ilmenite
			Goethite
			Tourmaline
			Purplish-grey augite

Description of Minerals

A. *Light separates*

Quartz. Quartz is the most abundant mineral forming between 30 and 50 per cent. of the separates. The grains are very clear and trans-

parent, and often well rounded. Small quantities of opaline silica are also present.

Feldspar. The dominant feldspar is anorthoclase which occurs as clear prismatic fragments or tabular grains. The grains have a fresh appearance throughout the profiles, in contrast to albite and microcline, which occur only in minor amounts, and are normally turbid and somewhat iron-stained. In amount the anorthoclase is fairly uniform throughout the sands, being 15–20 per cent. of the light minerals. In the profiles at Juja several grains of labradorite were noted.

Concretions. Black, irregular to very well rounded, iron-manganese concretions are fairly abundant throughout the profiles at all levels above that of the weathered rock: they appear identical with those described as occurring in the profiles of a tropical black earth and a grey earth from the Gold Coast (Stephen, 1953). The other main type of concretion is formed by the accumulation of calcium carbonate in nodules and granules at various levels in the soil profile (see profile descriptions).

B. *Heavy separates*

Opaques. Opaque minerals dominate the residues forming more than 60 per cent. of the heavy minerals in all the samples. The ore is mainly magnetite, with small amounts of ilmenite and goethite, the latter in the form of partially rounded concretions.

Epidote. Minerals of the epidote group are the commonest non-opaque minerals, varying from 10 to 15 per cent. in amount. Two main varieties are present, one greenish-yellow and well rounded with pitted surfaces, the other clear and transparent, colourless or yellow, and occurring in angular to subangular grains.

Pyroxenes. Aegirine and a green augite (or aegirine-augite), the characteristic pyroxenes of the underlying rocks, form from 3 to 5 per cent. of the heavy minerals. The aegirine occurs in 'stumpy' prismatic grains, averaging about 0·15 mm. in length, and showing a deep green to olive-green pleochroism. The grains are always very fresh in appearance. The augite (or aegirine-augite) resembles aegirine in colour, but occurs in more irregular prismatic grains up to 0·6 mm. in length, often showing markedly dendate terminations. Minor amounts of a purplish-grey augite are also present in the Juja profiles.

Amphiboles. Amphiboles are scarce at the Embakasi sites, but are common at Juja, where they make up 3–6 per cent. of the residues. Green hornblende is the commonest amphibole, and occurs as prismatic and irregular grains up to 0·3 mm. in length. Lesser amounts of blue-green hornblende, deep brown barkevikite, and colourless to pale green tremolite are also present. At Embakasi several irregular grains of an amphibole, pleochroic from reddish-orange to pale yellow-orange, have been noted: these probably correspond to the katophorite, described by Sikes (1939) as occurring in the lavas.

Biotite. Typical brown unweathered cleavage flakes are present in the lower layers of the profiles at Embakasi, but are scarce elsewhere.

Zircon, Rutile. Zircon and rutile are prominent accessories in all the soils. The former is in the form of both prisms with modified pyramidal terminations, and rounded grains. Rutile occurs as reddish-brown, amber, and yellow prismatic and irregular grains, and may show well-developed geniculate and polysynthetic twinning.

Sillimanite, Kyanite, Garnet, Staurolite. This group of metamorphic minerals is present in small quantities in all the profiles. Sillimanite and kyanite occur as colourless elongated grains, normally free from inclusions. The garnet is pale pink or colourless and angular, often with pitted or etched surfaces. Staurolite is in brown to yellowish-brown, slightly pleochroic, grains.

Tourmaline. Minor amounts of tourmaline were noted in the majority of the samples, as brown or blue prismatic fragments and irregular grains.

Apatite. Colourless, partly rounded, grains are present in small amounts in all the samples. Although apatite is a prominent accessory mineral in the underlying rocks, its scarcity in the soil suggests its limited stability even under alkaline conditions.

Sphene. Sphene is a rare constituent of the sands. The grains are brownish, angular, and fractured, and normally show incomplete extinction under crossed nicols.

The presence of porous vesicular rock beneath the 'puff site' and of massive compact rock beneath the 'shelf' at Embakasi suggested the possibility that a difference in rock character had led to differences in weathering products, and ultimately to profound differences in soil properties, but this is not substantiated at the Juja sites, where the rock beneath both the puff and the shelf is of uniform moderate porosity.

The mineralogical examination of the sands shows that the soils cannot be regarded as entirely residual from the underlying volcanic rocks. This is clearly shown by the presence of such minerals as sillimanite, kyanite, staurolite, &c., species that are characteristic of metamorphic rocks of gneissose type, and which occur at all levels in the soil profiles above that of the weathered rock. It is very difficult, however, to make any estimate of the amount of contamination, but it seems probable that these soils are mainly derived from the underlying rocks, but have had admixture of material of Basement Complex origin deposited on top, perhaps by wind transportation during past Interpluvial dry periods, which has been incorporated in the soils due to the churning action resulting from their shrinking and cracking properties.

Clay fraction. X-ray examination of the untreated clays ($< 2\ \mu$) showed that the main constituent was a montmorillonoid, which R. Greene-Kelly (1953) has shown to be a typical montmorillonite. The samples from Juja also contained small amounts of quartz and feldspar. Those from Embakasi contained a little kaolin and quartz as accessories. The kaolin may represent the metahalloysite that occurs in the underlying rock. There is no sign of an increased content of the accessories in the clay from the puff sites as compared with that from the shelf, nor is there any marked change in the relative proportions of the various constituents with depth.

Chemical and Physical Properties

In Table 2 are given some data illustrating the chemical and physical properties of the soils. The differences between the puff and shelf conditions are fairly well brought out. In each site the shelf soil tends to contain more clay, it shows a much higher swelling volume (Greene, 1948, p. 166), and contains distinctly more exchangeable sodium. At Juja the shelf soil is acid whereas the puff is slightly alkaline, the reverse is the case for the surface soil, at least, at Embakasi.

In general these results agree with those published by Hallsworth *et al.* The swelling test used in this study is not strictly comparable with the Keen-Raczkowski method, but the same trends are shown. The higher clay content with a larger proportion of exchangeable sodium confers a much higher swelling power on the shelf soils, although the subsoils in these Kenya profiles do not appear to swell as much as those described by Hallsworth and his colleagues.

TABLE 2

Analyses of Gilgaied Soils

(Air-dry basis on soil < 2 mm.)

	% *Clay* < 2μ	% *Silt* 2μ–20μ	*Sediment volume** H_2O c.c.	*Sediment volume** Na_2CO_3 c.c.	*pH* H_2O	*pH* M1/100 $CaCl_2$	*BEC* m.e./100 g.	*Exch.* Na m.e./100 g.
Juja Puff								
4106 0–6 in.	54	17	34	47	6·9	6·8	60·3	0·30
4107 6–15 in.	52	18	33	43	7·9	7·7	56·1	0·42
Juja Shelf								
4111 0–6 in.	64	11	31	59	7·4	7·1	63·5	2·92
4112 6–24 in.	62	13	42	61	8·2	8·0	62·6	4·47
4113 24 in.+	58	7	39	50	8·4	8·2	73·6	4·69
Embakasi Puff								
4115 0–18 in.	56	15	32	47	7·2	7·1	56·1	0·96
4116 18–27 in.	54	19	32	46	7·6	7·4	72·2	0·60
4117 27–36 in.	48	23	33	46	7·9	7·7	..	0·61
4118 36 in.+	40	11	30	39	8·0	7·8	61·6	0·70
Embakasi Shelf								
4120 0–15 in.	65	13	25	71	6·4	6·2	58·9	2·13
4121 15–30 in.	70	10	30	64	7·1	6·9	63·0	3·21

Soluble chlorides absent.

* H_2O the volume occupied by 20 g. soil shaken with 100 ml. water and left to stand overnight. Na_2CO_3 the volume after adding 5 g. Na_2CO_3, shaking and leaving to stand overnight.

Analyses by C. L. Bascomb.

Discussion

It is clear from the description of the mineralogy of the underlying rocks and the sand fractions of the soils that all the profiles have a common origin and would appear to result from the combined influence of climate and relief on the alkali-rich rocks. Under such conditions the rock weathers straight to montmorillonite (apart from any possible amorphous material). The rate of weathering appears to be relatively

slow and no great depth of soil has been formed. Although the amounts of calcium in rocks of the phonolite-trachyte type is low compared with that in basalts, the low rate of water percolation through such heavy clays, together with the high temperatures, would lead to accumulation and segregation of calcium carbonate. Wind-borne material from Basement Complex rocks could readily introduce the adventitious minerals found in the sand fractions.

These lavas have a high sodium content so that one would expect the resulting soil likewise to contain appreciable amounts in the exchange complex. Taking into account the various factors enumerated by Hallsworth *et al.*, it would appear that the black soils of the Athi Plains would be quite suited for the occurrence of gilgai phenomena. The descriptions given above and the laboratory data, incomplete as it is, would indeed seem to confirm that the marked 'island' or puff effect observed is gilgai of what has been called the normal type. The Tanganyika example described by Milne (1947), and referred to by Hallsworth *et al.* (1955, p. 30), is almost certainly gilgai, since the same phenomenon was seen by one of us at Ukiriguru (cf. Milne, 1947, p. 259), although this example was apparently missed by Milne. It would seem that the latter's description of 'islands' (ibid., p. 257) in the Hura Hura mbuga may also prove to be associated with gilgai conditions as judged by the soils near Old Shinyanga, Tanganyika, demonstrated to one of us by Mr. C. G. T. Morison. In addition to these and the Nyasaland example mentioned above, humps and hollows with sink-holes have also been seen on the Kafue Flats in Northern Rhodesia. Examples of gilgai phenomena have also recently been reported from the Lufira Valley in the Belgian Congo (Van Wambeke and Van Oosten, 1954). It would seem, therefore, that the phenomenon is widespread on the tropical black earths of East and Central Africa.

Acknowledgements

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Summary

An account is given of the occurrence of gilgai phenomena on tropical black earths in Kenya, with mention of examples from other parts of Africa. The present soils are derived from intermediate lavas which weather straight to montmorillonite. The mineralogy of the sand fractions is described, and chemical and physical data given to illustrate the high swelling power of the heavy clay soils.

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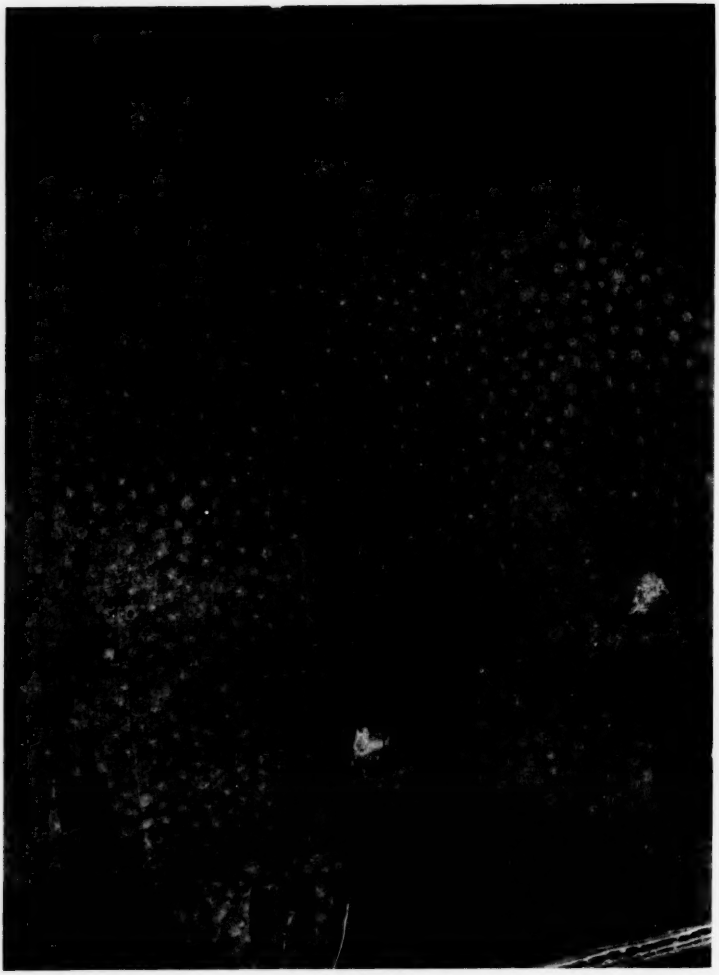
A. Maize growing on black clay soils of Athi Plains. Good growth on puff, poor on shelf. Stones are from deep ploughing.

B. Uneven growth of sisal on black clay soils of Athi Plains. The ground has been ridged in an attempt to obtain better growth

I. STEPHEN, E. BELLIS, *and* A. MUIR—PLATE I



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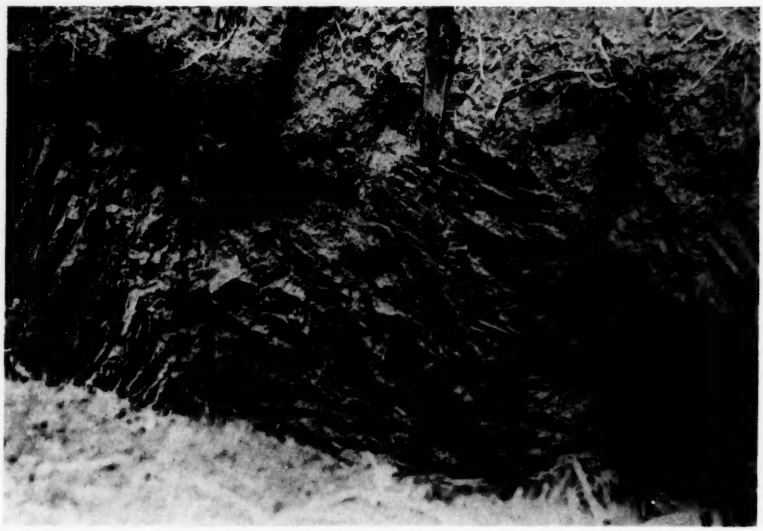
Air photo of part of the Embakasi area showing gilgai mounds

A. Puff soil from Tanganyika showing carbonate concretions



B. Shelf-type soil from Nyasaland showing massive blocky structure and large cracks

I. STEPHEN, E. BELLIS, *and* A. MUIR—PLATE III

MILNE, G. 1947. J. Ecol. **35**, 192.
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SOME MOVING SOILS IN SPITSBERGEN

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WITH TWO PLATES

Summary

A reconnaissance soil survey of an area of 160 sq. km. (60 sq. miles) was made in central Vestspitsbergen and the distribution of soils interpreted as a catena in which denudation has a more prominent role than in temperate regions; the more important soil characters were related to slope. The paper includes some observations on solifluction, polygonal soils, and perennially frozen ground. Finally the soils described are tentatively named according to the classifications of Kellogg & Nygard, and Kubiena.

Introduction

THE deserted mining settlement of Moskushamn on the south side of Isfjord was chosen as a base for the Aberdeen Spitsbergen Expedition during July and August of 1954, from where the soil survey and other field work were carried out in the mountainous block to the north-east.

Geology. The mountains are formed from an old erosion surface at about 950 metres by deeply incised cirque and valley glaciers which are accumulating above 500 metres, while glacier tongues descend to 200 or 300 metres above sea-level. Most of the district is underlain by nearly horizontal beds of Cretaceous sandstone, mudstone, and shale, with a few coal-seams. Some of the mountains are capped with lower Tertiary strata of very similar character. Jurassic rocks outcrop along the coast of Isfjord and in the western part of the area and comprise a uniform series of calcareous marine shales 600 metres thick. At Elveneset, in the north-east corner, are Triassic sandstones, marlstones, and limestones intruded by a sill of dolerite 30 metres thick, the only igneous rock encountered (Orvin, 1940).

I. *The Reconnaissance Soil Survey*

Factors in soil formation. Three environmental factors deserve comment. Firstly the whole of Spitsbergen is underlain by permafrost (perennially frozen ground) and therefore all soils have some degree of impeded drainage. Secondly, the profiles have developed in the active layer, i.e. the surface layer that thaws annually, and which is constantly churned by solifluction tending to inhibit the differentiation of horizons in the profile. Finally, the mean annual precipitation at Longyearbyen is only 20 cm. (8 in.); this, and the impeded drainage, occasionally combine to give inland occurrences of halophytic vegetation, and white efflorescences of salts on the ground.

The Soil Catena

In Spitsbergen the soil mantle is undergoing relatively rapid mass-movement; therefore it was reasonable to expect a relationship between soil morphology and slope, since all the material in any one profile must

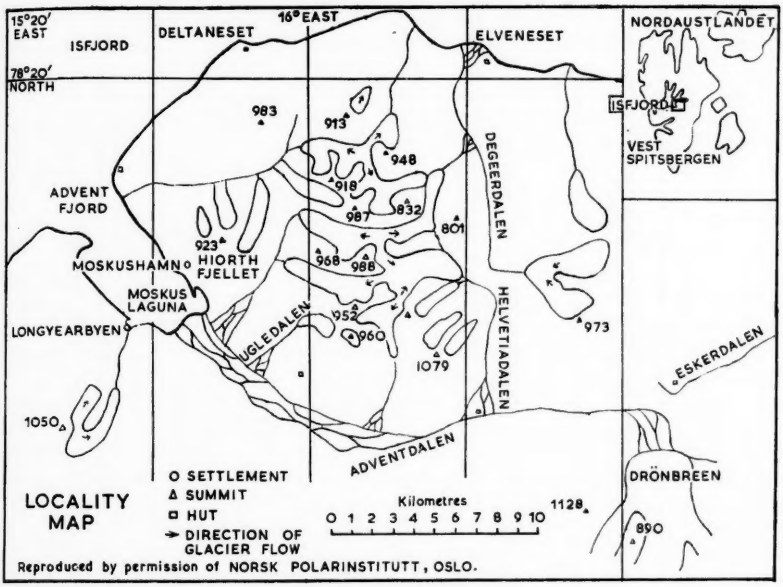

FIG. 1. Locality Map.

formerly have been part of a different profile higher up the slope. Of the various concepts of a soil catena, the one given by Milne (quoted by Bushnell, 1942) was found to be most applicable, because it stresses the role of denudation as well as considerations of slope and hydrology in determining soil morphology. The present catena is developed on a composition of Cretaceous sediments and superficial deposits derived from them; six divisions were made, each characterized by a polygonal or striped surface marking. Table 1 shows the relationships between slope and soil characters.

1. *Rock outcrops.* Because of the relatively soft nature of the rocks and the active congelifraction (mechanical frost weathering), there are few outcrops; where they do occur it is generally as tors, unstable pinnacles, and tottering heaps of blocks piled one upon another (Plate Ia).

2. *Scree.* This unit occupies by far the largest area owing to the mountainous character of the district. The slope is generally uniform at about 34°, and 60 to 90 cm. of rock rubble with an open texture overlie solid rock, which is frozen at a depth of 1 metre. A feature in striking contrast to British screes is that near the head of the slope the blocks are large, angular, and encrusted with lichens, but lower down they are smaller and free of encrusting lichens, and the voids are filling with a matrix of gritty loam. The fragments are derived by congelifraction of the underlying bedrock where it lies within the zone of annual freeze and thaw, and consequently there is no accumulation on the slope. In

TABLE I

A Table showing some of the Properties of each of the Series of the Soil Catena

Slope	*35°–25°*	*25°–12°*	*12°–4°*	*4°–½°*	*< ½°*
Soil series . . .	Scree	Striped	Solifluction	Mud polygon	Peat
Surface markings .	Almost bare scree	*Dryas* stripes and turf banked terraces	Various terraces and polygons	Mud polygons	Tundra polygons
Vegetation . . .	Very open *Papaver*, *Saxifraga* spp., &c.	Open striped and terraced communities. *Dryas octopetala* and *Salix polaris*	Closed community. Mosses, grasses, *S. polaris*, and *Cassiope tetragona*	Polygonal communities. *S. polaris*, mosses and grasses	Closed community in standing water. *Dupontia fisheri*, *Carex* spp., and mosses
Texture . . .	Open texture of stones	Stony, gritty loam	Stony clay loam	Clay loam	..
Drainage . . .	Free	Free—imperfect	Imperfect—poor	Poor—very poor	Very poor
Mottling . . .	Nil	Nil	Slight	Abundant	Nil
Depth of active layer .	100 cm.	120 cm.	60 cm.	50 cm.	50 cm. or more
pH	0–10 cm. 8·2* 46–60 8·39* 107 7·62* (frozen rock)	10–15 cm. 7·7 55–60 7·6 110–15 6·9 130–5 6·8 (permafrost)	litter 6·45 0–24 cm. 6·25 24–60 6·75 62–68 } 6·15 (p'frost) 90–94 } 6·6	litter 5·8 0–14 cm. 6·1 14–32 6·2 32–46 6·05 46–60 6·1 60–80 6·1 (permafrost)	2–6 cm. 4·99* 15–18 6·20*

pH readings marked * were made at the Macaulay Institute for Soil Research 3 months after sampling. The remainder of the pH measurements were made in Spitsbergen.

contrast, temperate and arid screes are formed by fragments falling from a cliff and accumulating on the slope below. The scree has a very open community of *Papaver dahlianum*, *Saxifraga oppositifolia*, *S. cespitosa*, *S. cernua*, *Oxyria digyna*, and *Poa* spp.

The author was struck by the similarity between this scree material and the shattered rock overlying Silurian greywackes in the south of Scotland, which on 15° to 25° slopes forms the parent material of the Ettrick Association of soils.

3. *Striped soils.* Lower down the angle of slope decreases and where it is about 25° *Dryas octopetala* establishes itself as a striped community; longitudinal stripes of bare and *Dryas*-covered scree alternate about every 1½ metres across the slope (Plate Ib). As the slope diminishes, individual stripes become shorter and less regular, the gravelly stripes finishing suddenly as semicircular lobes of mobile gravel; finally, where the slope is about 15°, these lobes dominate the pattern, forming crescentic terraces of bare gravel 1 or 2 metres in diameter and separated from each other by short walls of *Dryas octopetala*, *Salix polaris*, and mosses. In section it is seen that the gravelly stripes and terraces are not due to a differential sorting of the underlying material, which is a gravelly loam. The soil profile beneath the *Dryas* and *Salix* has 5 cm. of litter resting on a dark grey stoneless loam 12 cm. deep; beneath this is the gravelly loam which extends to the surface of the scree stripes. Often a stratification of sandy and peaty bands is present, reflecting the mobility of the soil. Permafrost was found at a depth of 90 to 130 cm.

4. *Solifluction soils.* This name was chosen for want of a better one since the scree and striped soils also show evidence of solifluction. The series is characterized by smooth slopes between 12° and 4° with a strong micro-relief comprising small pits 50 cm. deep, small irregularly shaped terraces of bare mud and tussocks of moss and heather. *Salix polaris* and *Dryas octopetala* are the dominant species with grasses and mosses such as *Alopecurus alpinus*, *Drepanocladus uncinatus*, and *Aulocomnium turgidum* forming a closed community except for occasional terraces or polygons of bare mud; in slight depressions the arctic bell heather (*Cassiope tetragona*) is dominant. The following profile occurred on an 8° slope beneath *Dryas octopetala* and *Salix polaris*. Munsell colour nomenclature is used throughout the profile descriptions.

8–0 cm. Reddish-black (10 R 2/1) undecomposed litter of mosses and *Salix* leaves; pH 6·45.

0–24 cm. Very dark grey (10 YR 3/1) heavy loam; weak granular structure; frequent angular fragments of sandstone; no mottling; pH 6·25; very moist; merging to:

24–60 cm. Very dark grey (10 YR 3/1) clay loam; blocky structure; frequent stones; roots to 35 cm.; no mottling; pH 6·75; wet, becoming very wet at 50 cm.; sharp boundary.

60 cm.+ Frozen clay loam with 25 per cent. clear ice arranged in laminae parallel to the surface and up to 6 mm. thick. At 65 cm. pH 6·15, at 92 cm. pH 6·6.

Fabric analysis of the block material in this pit (Fig. 2 *b*) shows a more random arrangement of the fragments than is found in the scree (Fig. 2 *a*), but the most interesting feature is that there is a maximum tendency

for the stones to dip *into* the slope, rather than down the slope, suggesting an imbricate fabric as in the arrangement of stones in the bed of a stream. One could conclude that the soil is moving by flow and not by the downward movement of individual fragments, or creep.

5. *Mud polygon soils.* Two contrasting types of mud polygon are common on slopes less than 4°: one, the mud boil of Müller (1947), has

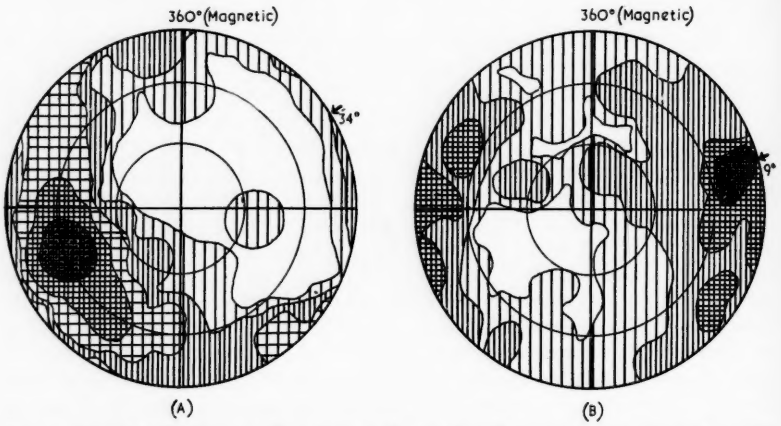

FIG. 2. Petrofabric diagrams showing the disposition of stones in two types of moving soil. *a.* Scree (contours 1, 3, 6, 12, 25%); *b.* Solifluction soil (contours 2, 4, 8, 10%). The slopes are marked in degrees. *Method of fabric analysis.* The orientation of the longest axes of 250 rock fragments was recorded; the dip of each was measured with a clinometer, and the azimuth with a magnetic compass in degrees clockwise from magnetic north. Each pole was plotted on a Schmidt net (Lambert's equal area projection), and contours were drawn enclosing areas in which a given number of poles lie within a circle whose area is 1% that of the projection.

a flat mud centre 80 to 120 cm. in diameter bordered by narrow ridges of moss and *Salix polaris*, and is considered to be the normal development in the catena (Plate IIa). The other, the soil polygon of Elton (1927), is an elliptical mound of bare mud with a longer axis of about 1½ metres directed in the line of slope; the shorter axis is ¾ to 1 metre. The mud centre is elevated 25 cm. above the surrounding hollows, where mosses grow on a deep litter 20 cm. thick (Plate IIb). Both types of mud polygon show in section (Fig. 3) that the mossy litter protects the frozen subsoil which forms a corresponding ridge, and that the upper surface of the permafrost is therefore depressed under the centres of the polygons.

Salix polaris is the dominant species of this series, occurring with a wide variety of herbs and mosses, e.g. *Alopecurus alpinus*, *Saxifraga hirculus*, *Polygonum viviparum*, *Ranunculus sulphureus*, *Drepanocladus uncinatus*, *Aulocomnium turgidum*, and *Camptothecium nitens*. A profile is described from a site without mud polygons.

10–0 cm. Litter, undecomposed debris of mosses and *Salix*; pH 5·8.
0–14 cm. Very dark grey (7·5 YR 3/1) loam; granular structure; occasional stones; ochreous mottling along old root channels; pH 6·1; moist; merging to:

14–32 cm. Very dark grey (5 YR 3/1) clay loam; granular structure; no stones; mottling as above; pH 6·2; merging to:

32–46 cm. As above but structure changing to small rectangular blocks about 4 mm. in diameter; pH 6·05; very moist; merging to:

46–60 cm. Dark grey brown (10 YR 4/2) clay loam; small angular blocky structure; a few roots penetrating this horizon; no mottling; pH 6·1; very wet; sharp boundary.

60 cm.+ Frozen clay loam, the amount of ice increasing with depth to about 85 per cent.; pH 6·1.

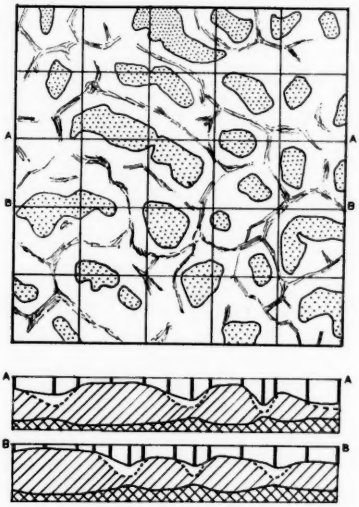

FIG. 3. Plan and section of mud polygons at Moskushamn. The total area is 100 sq. metres. Depths of the active layer were measured at the places marked with a double line in the sections. Bare mud is marked by stippling; mossy grooves by bundles of thin lines, and by broken lines in the sections; double hatching represents the permafrost, and single hatching the active layer. Vertical scale exaggerated × 2.

6. *Peat.* In the areas mapped as peat the plant litter has accumulated sufficiently for its lower layers to be perennially frozen, as in waterlogged sites in Adventdalen. The accumulation must be due to low microbiological activity rather than to rapid growth of plants. The ground has water lying at the surface in summer and is often coloured red by an alga; it supports a prolific growth of grasses, sedges, and mosses, including *Dupontia fisheri*, *Eriophorum scheuchzeri*, *Carex subspathacea*, *Aulocomnium turgidum*, and *Camptothecium nitens*.

Aerial photographs show that the peat has polygonal markings 20 or 30 metres in diameter; on the ground the dark margins of these polygons correspond to browner mosses where the depth to the permafrost table is greater.

Other Soil Catenas

There are several geological and physiographical factors interfering with the sequence of soils described; indeed it is only in Adventdalen that the series occur in order consistently. The most frequent of these factors is the formation of alluvial fans by streams descending from the mountains and discharging their loads where the gradient changes abruptly. A detailed survey of the large fan emerging from Ugledalen shows a sequence of soils and plant communities comparable with that of the main catena, but in this case the slope is uniformly 3° to 4° and the soil morphology is controlled by age and distance from the river bed

In parts of Degeerdalen, Helvetiadalen, and upper Adventdalen hillsides formed of Jurassic shales have a different catena: the shale breaks up into small flakes in a silty matrix forming a less stable soil, consequently slopes as little as 25° are virtually bare of vegetation. Along the coast of Isfjord is a prominent raised beach 20 to 30 metres above sea-level, on the gently sloping surface of which are gravels sparsely colonized by *Dryas octopetala*, although in the normal catena the same slope would have mud polygon soils.

Saline soils. Saline soils occur on recent marine alluvium in three kinds of site: near the sea-shore, along the youngest raised beach in Adventdalen, and alongside 'pingos' which are mentioned later. From a distance the sites appear red owing to the presence of the obligate halophyte *Puccinellia phryganodes*; other characteristic species are *Stellaria humifusa*, *Carex ursina*, and *C. subspathacea*. Soil profiles examined were immature, the only distinguishable horizon being efflorescences of salts at the surface; the subsoil is silt or fine sand with a conspicuous small angular blocky structure, though in a wetter site the structure is cloddy or prismatic. In both sites there is ferruginous mottling. Efflorescences of salts were seen on several freshly exposed surfaces, e.g. on moraines and alluvium. Some crystals from near the sea-shore at Moskuslaguna were shown by X-ray powder technique to be Na_2SO_4.

Alluvium. Fluviatile alluvium is being deposited in the larger watercourses; the Advent river, for instance, is broken into many braided channels wandering over a bed of sand and gravel about a kilometre wide and practically devoid of vegetation.

II. *Soil Mobility in a Periglacial Climate*

The correlation between climate and the processes of denudation expounded by Penck (1953) is particularly evident in the Arctic, where frost is the dominant agent in rock-reduction and in mass-movement, to use Penck's terms for the two chief components of denudation. Both processes have received special names when acting in a periglacial environment: *congelifraction* was introduced by Bryan (1946) for the mechanical breakdown of rock caused by water freezing in its joints and pores, while *solifluction*, although defined by Andersson (1906) to include nearly all forms of mass-movement, is currently restricted to movements

influenced by frost heaving or the presence of permafrost (Eakin, 1916). Solifluction is a composite process divisible into soil creep and soil flow.

Soil creep. Soil creep is the slow downslope movement of individual particles and aggregates of soil due to gravity assisted by soil flora and fauna, agriculture, and volume changes associated with wetting, drying, and frost heaving. The last is the most important in a periglacial climate. Taber (1930) showed that when soil freezes in an open system, needle-shaped crystals of ice grow normal to the cooling surface by drawing up capillary water; stones and earth are lifted normal to the surface and, when the system thaws, collapse vertically under the influence of gravity, giving a net downslope movement.

Soil flow. Profiles examined in the solifluction and mud polygon soil series have an extremely wet horizon 5 or 10 cm. thick at the base of the active layer. It is thought that this layer acts as a slip plane, allowing movement of the soil *en masse*; the position of the horizon is at different levels during the summer thaw, so that maximum movement takes place at the surface, as in viscous flow. It is therefore difficult to decide whether the movement should be classed as flow or slip (Sharpe, 1938). Further evidence of soil flow is the presence on low-angled slopes of cracks tens of metres long and a few centimetres wide; it was established that the opening of one such crack at Moskushamn was completed when the expedition arrived on 22 July, suggesting that soil flow is confined to early in the thawing season.

III. *Polygonal and Striped Soils*

The formation of polygonal patterns in nature can be attributed to processes of contraction and of expansion, suitable examples being columnar basalt and the pith cells of a vascular stem. Two types of soil polygon caused by contraction are the perennial desiccation polygons (fissure polygons) forming on freshly exposed surfaces of sand and silt, and the large tundra polygons (see below). Most other soil polygons result from the juxtaposition of expanding units of differential frost heaving or congelifraction. Five types of polygon of this category were seen, and for each there is a homologous striped pattern on steeper slopes; in addition to slope, vegetation and texture are important in determining the type of surface marking (Lundqvist, 1949). The absence of soil fauna appears to contribute to the persistence of the structures, since in temperate soils any orientation of stones to form polygons would be obliterated by moles and earthworms.

Tundra polygons. These large markings, 20 to 30 metres in diameter, are evident in most aerial photographs of tundra. Leffingwell (1915) concluded that intense cooling of the land surface causes polygonal cracks to open and fill with ice which prevents them from closing in summer. In Degeerdalen an ice wedge beneath the border of a tundra polygon penetrated raised beach gravels to a depth of 6 metres, and tapered upwards from a few centimetres to 30 cm. near the frost table. Polygons with both raised and depressed centres were seen, the former

in sites that are poorly or imperfectly drained by British standards, while the latter are present in very poorly drained sites.

The catenary distribution of surface markings. It was found in the course of the soil survey that each surface marking characterizes a given site, and can therefore be used to identify the soil profile beneath. Each type of marking is thought to be derived from that occurring higher up the slope in the following way.

Dryas octopetala begins to colonize the moving scree as the slope decreases to about 25°: an isolated plant of *Dryas* creates a stable area behind it, allowing rapid growth of the community down the slope in the form of a stripe; on either side the scree moves faster than elsewhere on the slope, preventing the *Dryas* from extending laterally, so the next plants colonize a short distance away on either side. A repetition of this sequence results in a regular series of parallel stripes. When the slope decreases to about 15°, individual stripes give place to gravelly turf-banked terraces in a manner already described; the terraces are subject to frost heaving causing a slow downhill motion and maintaining the distribution of vegetation and bare gravel (Sigafoos and Hopkins, 1952). At the lower boundary of the terraced soils (12°) soil flow gradually replaces creep as the method of mass-movement, and many of the terraces are carried down the slope into the area of the solifluction soil series, while others become overgrown; the active layer is shallower here, and beneath the turf at the margins of the terraces appear corresponding ridges in the upper surface of the permafrost. Once this has happened the system becomes self-aggravating. Moisture accumulating in the depressions in the frost table produces greater heave when the active layer freezes in winter, a process called suffosion (Nikiforoff, 1932); in the present circumstances it results in the mud polygons described.

IV. *Observations on Ground Ice*

The quantity of ice in the permafrost seemed to vary with the texture and wetness of the active layer; thus beneath very poorly drained silty clay the permafrost was estimated to be 85 per cent. ice, while some frozen sand had only about 10 per cent. of ice. The structure of the ground ice varied with the texture of the frozen material: in silt or clay loam the ice occurs in lenses and sheets parallel to the surface, and from 0·5 to 5 mm. thick (Fig. 4). In frozen gravel the ice forms a film around stones, rather thicker on the underside, while in frozen shale the rock is ramified by thin veins of ice along joint and bedding planes. These observations confirm those made by Taber (1943) in Alaska. Some of the ice structures were recorded by holding paper over a flat surface and rubbing with a soft pencil (Fig. 4).

The depth of the active layer depends on its texture and wetness, the altitude of the site, and the degree of surface insulation by vegetation or snow; it is less under a thick mat of vegetation, and greater where there is free drainage, light-textured material or at low altitudes. The greatest depth measured was 130 cm. in a striped soil, while in coarse rock debris at 900 metres the active layer is only 35 cm. thick. Beneath

patches of snow the ground is frozen to the surface. Apart from this the active layer is as little as 15 cm. thick where there is a thick plant litter, as, for instance, under the mossy grooves or banks between mud polygons. Standing water is a bad insulator and in flushes or peat bogs the permafrost is at a depth of 60 to 80 cm.

Other ground ice structures seen were ice wedges forming the margins of tundra polygons, and pingos (Müller, 1947).

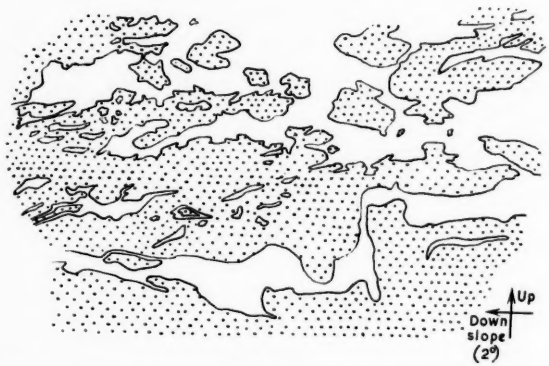

FIG. 4. Distribution of ice in permafrost. Clear ice is shown white, and the mineral soil is stippled. The drawing is traced from a rubbing. $\frac{2}{3}$ natural size.

V. *Classification of the Soils*

Spitsbergen lies within the zone of tundra soils, but due to strong relief and instability of the ground the dominant soils are azonal lithosols, regosols, and alluvial soils. The zonal soil is taken to be represented by the solifluction and mud-polygon soil series, which differ only in maturity and drainage. A generalized profile is:

A_{00}	5–0 cm.	Reddish-black unhumified litter of *Salix polaris* and mosses; pH 6·0.
A_1	0–15 cm.	Very dark grey loam; crumb structure; high content of organic matter; ochreous mottling along root channels; pH 6·3; moist; merging to:
BG and CG	15–60 cm.	Very dark grey clay loam or silt loam; small subangular blocky structure; ochreous mottling associated with peaty inclusions; pH 6·3; very moist, becoming very wet in lower 10 cm.; sharp boundary.
D	60 cm.+	Perennially frozen clay loam or silt loam, much ice segregated in bands and lenses.

The nearest soil to this, described in the literature, is the 'tundra soil with permafrost' of Kellogg and Nygard (1951). The following scheme shows the soils classified according to the nomenclature of Kellogg and Nygard (1951) and Kubiena (1953).

Soil Series	*Kellogg & Nygard* (1951)	*Kubiena* (1953)
Rock	Lithosols—azonal	—
Plateau Frost Debris		Arctic Hamada Rawmark
Scree (Cretaceous and Jurassic)	Regosols—azonal	Common Arctic Rawmark
Striped soils		Structure Rawmark
Solifluction soils	Tundra soils—zonal	—
Mud Polygon soils		
Peat	Bog—intrazonal	—
Saline soils	—intrazonal	Solonchak
Alluvium	Alluvial soils—azonal	—

The application of the catena concept to soils of the tundra zone is not entirely new; without actually using the word 'catena', Kellogg and Nygard (1951) describe an association of soils in the north and west of Alaska in which lithosols occur on the mountain tops and upper slopes, tundra soils on the lower slopes, while depressions and valley bottoms have bog and alluvial soils respectively.

Acknowledgements

The Aberdeen Spitsbergen Expedition was led and largely organized by Dr. E. A. Fitzpatrick of the University of Aberdeen, and the author would like to express his appreciation of the excellent arrangements that were made. Much of the field work, particularly the soil survey, was carried out in company with O. Einevoll of the Norges Landbrukshögskole, Norway, and it is hoped that a fuller account of the soils incorporating a map and analytical data will be published jointly. The author also wishes to thank the other two members of the expedition for their help, A. C. Crundwell for his careful identification of the plants, and T. E. Fletcher for measuring pH's in the field.

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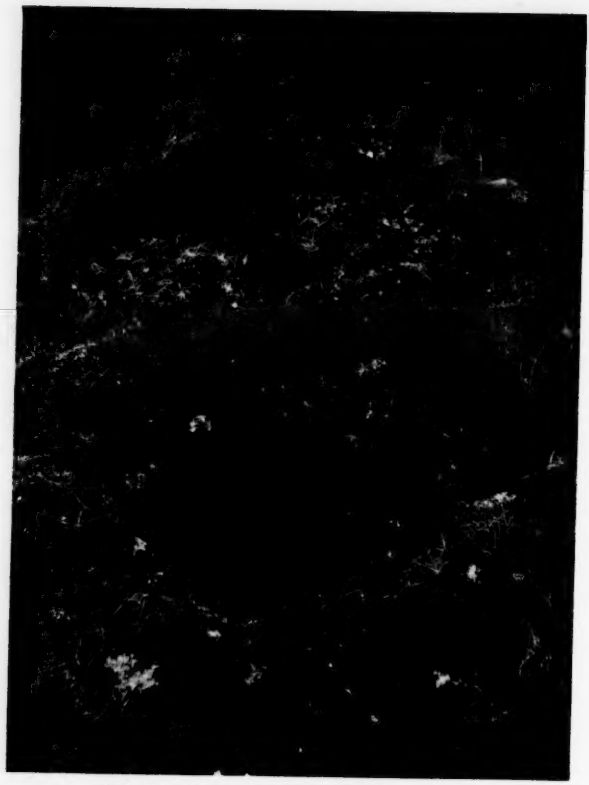
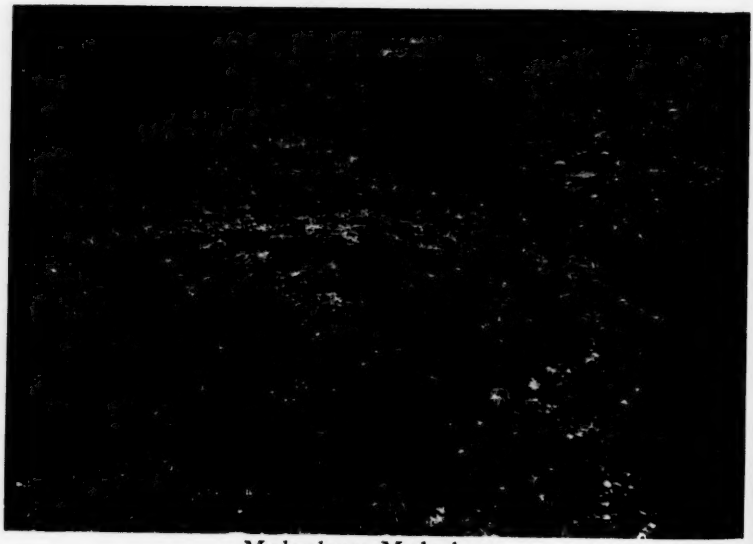
Unstable pinnacles 5 metres high at 900 metres on the north side of Altbreen

Stripes of *Dryas octopetala* 18° slope

J. SMITH—PLATE I



'Mud boil' on the shore of Adventfjord



Mud polygon, Moskushamn

J. SMITH—PLATE II

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ALPINE SOILS OF THE ROCKY MOUNTAINS[1]

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Summary

A field and laboratory study was made of soils developed in the alpine region of the Rocky Mountains. The region is a grassland above the general elevations of 10,500 ft. in Wyoming, 11,500 ft. in southern Colorado. Cold inhibits soil development.

Three groups of soils occur. Their gross characteristics are determined by drainage and variations in parent rocks from which the soils developed. The groups are described and given the names of Alpine Turf, Alpine Meadow, and Alpine Bog soils.

Only the Alpine Turf soils were studied in the laboratory. They are characterized by an organic-carbon content of 5–20 per cent. in the surface 5–7 in. and coarse, gravelly, or sandy textures throughout. The largest amounts of silt and clay occur in the surface. The range in pH is from 4·5 to 8·4, depending on the kind of parent rock, but no marked variations occur in any horizon of any soil. Preliminary studies revealed the presence of some of the common clay minerals in the fine soil fractions. This was taken as evidence that these soils are starting on the normal course of soil development. The morphology is simple, consisting of an A–B–C profile. Horizons are more distinct in the turf soil than in either the meadow or bog soils.

Introduction

THE region above tree growth in the Rocky Mountains occupies about 4,450,000 acres (Schwan and Costello, 1951). It is a region in which extreme cold inhibits soil development. Knowledge of these soils should contribute to a better understanding of the processes of soil genesis.

The object of this study was to determine morphological characteristics and geographical relationships of the soils; to supplement this with laboratory analyses as a basis for developing an understanding of the genetic processes; for developing a classification of soils in this zone.

The Alpine Landscape

In this paper the term 'alpine' is used inclusively as a noun to denote the region or landscape as a whole above normal tree growth and below permanent snow.

Alpine borders

The Rockies in Colorado and Wyoming have no permanent snowline. The lower border, a jagged line that varies in elevation locally as much as several hundred feet, is near 10,500 ft. elevation in northern Wyoming and above 11,500 ft. in southern Colorado. The line is locally established

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[2] The writer expresses his appreciation of the helpful suggestions and assistance in field sampling received from Professor R. J. Muckenhirn under whose general supervision this work was done.

by strong winds, tree damage by wind-driven snow and ice crystals, bare rock exposures, creeping masses of loose rock, landslides, snowslides, persistent snowbanks, very steep slopes, and fires.

Climate

Reliable climatic data for the Rocky Mountain alpine are meagre. Data from U.S. Army (1874–90) and U.S. Weather Bureau (1930) records show a range in annual precipitation from 29 to 41 in. for three stations and in mean annual temperature from 27° to 19° F. for two stations. The proportion of precipitation as snow and as rain is not known, but Whitfield (1933) found that precipitation was greater at lower than at higher elevations.

Temperatures are lower at higher elevations. Freezing is frequent even in summer. Daily temperature variations are extreme and change rapidly. Diurnal temperature changes range from 30° to 48° F. Wind velocities exceeding 100 miles per hour have been recorded.

Frozen subsoils

The depth to permafrost is not uniform, and the relation of depth to steepness of slope, exposure, and drainage is not fully known. Ice is found within a foot of the surface under peat in some marshes in late summer. It has been found in newly exposed mine pits and new road cuts at 5 to 8 ft. beneath well-drained soils in September. Construction of major highways has likewise exposed large areas of ground ice. Miners report that the summer thaw penetrates 5 to 7 ft.; that the bottom of the frozen layer occurs from 60 to 400 ft. beneath the surface. This frozen subsurface may affect soil development appreciably.

Geology

The Rockies originated as an upthrust through several thousand feet of sedimentary rocks. Subsequent erosion exposed primary rocks, dominantly granites, and the accompanying metamorphic rocks, but pockets of sedimentary rocks, such as shale, limestone, sandstone, and quartzite, remain in spots. Basalt, andesite, and rhyolite also occur. The many rocks give rise to a variety of soil parent materials and are a major factor accounting for differences in alpine soils, especially on well-drained areas.

Topography and erosion

The alpine is a landscape of steep topography, with 52 peaks having elevations above 14,000 ft. Some areas have gentle slopes where soils develop under slow rates of erosion. Drainageways are entrenched in lower parts of the zone. A wide variety of micro-landforms exists, resulting in complex soil patterns.

Surface erosion by wind and water and deep-seated mass movements of materials on steep slopes are common. Wind erosion occurs on the tops of prominent peaks and in passes exposed to a prevailing wind direction. Water erosion is not important where the surface is protected by a tough sod, but below snowbanks, on overgrazed lands, and on

windswept areas it is active. Gully erosion is rare. Dense willow fields, where ungrazed, protect basins from gully and surface erosion.

Vegetation

In aspect, the alpine is a boulder-studded grassland. Inspection reveals groupings of species governed by elevation, exposure, and local soil variations. In the bent timber zone the main species are *Picea engelmanni*, *Abies lasiocarpa*, *Pinus flexilis*, and *P. aristata*. Well-drained soils are covered by the sedge *Kobresia bellardi* (All.). Other common plants are *Carex drummondiana* Dewey, *Geum rossii* (R. Br.), *Avena mortoniana*, *Polemonium viscosum* Nutt., and *Rydbergia grandiflora*. The latter two are more common on the drier, rock-studded areas. Most soils are occupied by several species of willow (*Salix* spp.) and sedges (*Carex* spp.) and *Deschampsia caespitosa* (L.) Beauv. Plant nomenclature follows that of Harrington (1954).

Erosion is reduced by the dense tough sod under alpine plants. Roots in the soil are well preserved on all areas, probably because of low temperatures that restrict microbiological activity. Digging and burrowing animals are scarce. Insect larvae and angleworms have never been observed although the former must be present. Therefore, the opportunity for mixing of soil and organic residues is not as great as at lower elevations. Few roots extend below 25 or 30 in. and most are concentrated in the surface 5–7 in. of well-drained soils.

Because of wet conditions, low temperatures, and shallow ground ice, plant residues accumulate to form bogs in places. These areas are distinctive but not extensive.

Soil Morphology and Classification

Field work resulted in the establishment of three broad classes above the series category, namely, Alpine Turf, Alpine Meadow, and Alpine Bog soils. These groups are equivalent to the Great Soil Groups. Each is defined and described below.

Alpine Turf soils

These are black to dark brown mineral soils developed from mineral parent materials of any character, internally and externally well drained and having well-defined horizons, with the A horizon being divisible into two parts. The surface soil contains 5–20 per cent. organic carbon. These soils occur on the higher, convex, well-drained slopes. Permanently frozen layers may be found within 6–8 ft. of the surface.

A description of the modal profile follows:

A_{11} Thickness: 0 to 2 in. Commonly thin but may be absent.
Colour: Black to very dark grey.
Texture: Sandy loam with very high content of partially decomposed organic residues such as roots and stems.
Structure: Weak, medium granular.
Reaction: Calcareous to moderately acid (pH 5·0).

Note: Filled with many live and dead coarse roots, plant stems, and leaves. Often gravelly. This horizon is usually included with the A_1.

A_1 Thickness: 4 to 7 in.
Colour: Dark grey, dark greyish-brown, or black.
Texture: Sandy loam. Often much sand, gravel, and some large stones.
Structure: Weak, fine, or medium granular.
Reaction: Calcareous to strongly acid (pH 4·5).
Note: Held together with a dense mat of tough roots—a sod or turf. High in organic matter. Lower transition boundary 1 to 2 in. wide.

B Thickness: 7 to 15 in. Rarely deeper than 15 to 20 in. from surface.
Colour: Very dark brown, dark greyish-brown, or brown.
Texture: Sandy loam. Often much gravel and some large rocks.
Structure: Very weak, small granular, or no structure.
Reaction: Calcareous to strongly acid (pH 4·5).
Note: Roots decreasing in quantity. Colours lighter and sometimes show effect of parent materials. Gravel and many rocks.

C_1 A light coloured thin (3 to 5 in.) transition from the A_3 to the C but more like the C. Low organic-matter content. Loose, open, and gravelly. Underside of rocks usually stained black.

C_2 Colour: Brown, pale brown, or light yellowish-brown. Depends on parent material.
Texture: Loamy sand. Many large rocks and much gravel.
Structure: None.
Reaction: Calcareous to strongly acid (pH 4·5).
Note: A few roots to 24 to 30 in. Underside of rocks stained black.

Roots mat beneath stones and form a distinctive black organic residue. This distinctive feature rarely occurs in the meadow soils. Summer showers may also carry organic residues that collect and remain as dark films. This film and small stalactites on the underside of rocks in soils from limestone suggest that moisture is not abundant in these soils in summer.

'Alpine Turf' was chosen as a name for these soils because of the distinctiveness of the vegetation type and the extreme density and toughness of the sod that blankets the surface.

Table 1 shows the general location, parent rock type, and elevation of areas where samples of turf soils were taken for analyses.

TABLE 1

Location, Parent Rock, and Elevation of Areas studied in Colorado Rockies

Location	*Parent rock*	*Elevation (feet)*
Buffalo Peak—Mosquito Range (30 miles south-east of Leadville)	Basalt	12,400
Rollins Pass—Front Range (50 miles north-west of Denver)	Schist (biotite, muscovite)	12,000
Weston Pass—Mosquito Range (25 miles south-east of Leadville)	Granite (biotite)	12,400
Weston Pass—Mosquito Range	Quartzite	12,800
Wheeler Mt.—Mosquito Range (20 miles north-east of Leadville)	Shale	12,500
Wheeler Mt.—Mosquito Range	Limestone	12,600
Baldy Chato Mt.—La Garita Range (30 miles north of Creede)	Andesite or dacite	12,500

Alpine Meadow soils

These are black or very dark brown mineral soils developed from mineral parent materials—usually local sediments—under imperfect to poor internal drainage. They have A–C profiles with varying degrees of subsurface mottling. The organic content is usually greater than in the turf soils, but the soils are not peaty. Depths to permanently frozen layers may be deep or shallow. The meadow soils dominate the lower slopes and concave positions of the landscape where surface run-off is retarded and where seepage from higher areas may collect during the summer. A specific profile is described as follows:

Parent rock: Granitic alluvium and glacial till.
Site: Lower slope.
Topography: 15 per cent., slightly concave slope; elevation 12,400 ft.
Vegetation: Sedge and willows.
Layers:

1.	0–4 in.	Mat of leaves and twigs.
2.	4–6 in.	Very dark grey, soft, organic layer; pH 5·9; many gravels.
3.	6–12 in.	Dark greyish-brown; gravelly loam; rocky; considerable organic matter; pH 5·8.
4.	12–19 in.	Dark grey; gravelly loam; low organic matter; rocks; pH 5·6.
5.	19–27 in.	Dark greyish-brown; gravelly loam or loamy gravel; rocks; pH 5·2.
6.	27–31 in.	Dark olive-grey; gravel and sand; pH 5·3.

The term Alpine Meadow is given to this group of soils and is restricted to those soils developed under imperfect to poor drainage where the aspect is that of a moist meadow throughout the year. In the literature the term has been given a more inclusive definition. As defined here, it should not be confused with the term *mountain meadow* which commonly refers to relatively flat, moist, or wet areas below timberline.

Alpine Bog soils

These are black or brown highly organic and peaty soils developed in bogs and wet areas. They have A–C profiles with highly mottled subsoils. Often they are stratified and strongly reworked by frost action. Dense silty layers or lenses are common in deeper parts. Frozen subsoils occur at various depths and may be very shallow. The bog soils occur in any place where waters are ponded for long periods or where the soil is kept wet. A bog-soil profile has the following characteristics:

Parent material: Organic residues mixed with mineral sediments.
Site: Bog.
Topography: Level to depressional; elevation 12,500 ft.
Vegetation: Sedge and willows.
Layers:

1.	0–8 in.	Dark brown to black, mixed peat and mineral materials; pH 5·1.
2.	8–25 in.	Dark grey lenses and layers of tough, fibrous peat.
3.	25 in.	Gravel, rock, and sand. Frozen soil at 30 in.

In the above classification no provision is made for 'skeletal' soils and areas swept bare by wind, water, or gravity. These are areas of landscape degradation and are not considered soils.

Other classifications

This study proposed three classes in the Great Soil Group category for the alpine soils, but other investigators have expressed different ideas. In some instances, all soils of the alpine have been placed in one group and called Alpine Humus soils (Braun-Blanquet, 1932, p. 257). Kellogg and Nygard (1951, p. 33) used the terms Alpine Meadow and Mountain Meadow, but their Mountain Meadow group also includes soils developed below the alpine. Thorp and Smith (1949, p. 118) suggested 'Alpine Meadow' as the Great Soil Group name. Other terms such as 'tundra-like' and 'mountain tundra' have been used. Jenny (1930, p. 108) used the term 'Alpine Humus soils' and listed the following inclusions in the group (translation by Jenny[1]):

> Near and especially above timberline is found a variety of soils which may be grouped under the general name Alpine Humus soils. They include the so-called mountain meadow soils (but not those designated as such in the Rocky Mountains, which, I believe, are filled-up ponds and lakes and are hydromorphic), peaty mountain-top soils, raw-humus soils, tundra-like high-mountain soils, alpine-mull soils, grass-mull soils, pioneer-vegetation soils, grass-mor soils, dry-peat mountain soils, alpine humus, lichen humus (Flechter), alpine mull, etc.

Jenny (1930, p. 110) quotes Leiningen as defining alpine humus soils in the following manner:

> Alpine humus includes all characteristic alpine deposits of humus (excluding bogs), which are developed in place (authochthon) and which have only as much fine material as can be accounted for by the humus-forming materials and dust. The greatest part is decayed, but sometimes is raw humus. The colour is bright but grades through dark brown and black. With increasing lime content the alpine humus has a darker colour. The largest deposits of alpine humus are over limestone. (Translation by Retzer.)

Jenny (1948) used the term Andino Humus soil for a soil encountered in the Andes of Colombia. The term is roughly equivalent to the Alpine Turf soils of this study except that the soil is much more acid and has almost double the carbon content.

The use of the term 'meadow' is objectionable for all alpine soils other than bogs because it implies moist, damp conditions (at least in this part of the world). Indeed, both the terms 'alpine meadow' and 'mountain meadow' have been defined as intrazonal (Kellogg and Nygard, 1951; Thorp and Smith, 1949). This is not in line with the findings of this study. The term 'alpine humus soils' is too inclusive by definition.

The three soil groups proposed in this study are clearly recognizable, extensive geographic units. They are taxonomic units in which local drainage dominates even the strong influence of parent materials in soil formation.

Analyses of Turf Soils

Data presented below deals only with Alpine Turf soils developed from different parent rocks.

[1] Correspondence in April 1952.

Some physical and chemical properties[1] of six turf soils are given in Table 2.

Most surface soils are dark brown or black, while deeper layers are brown or yellowish-brown. Soils from shale and limestone have high pH values that increase with depth. Acidity of soils from other rocks

TABLE 2

Some Characteristics of Six Alpine Turf Soils from Various Parent Rocks

Parent rock horizons (*inches*)	*Colour* (*air dry*)	*pH*	*Organic carbon* (%)	*Mechanical separates*† *Gravel* > 2 mm. (%)	*Sand* 2–·05 mm. (%)	*Silt* ·05–·002 mm. (%)	*Clay* < ·002 mm. (%)
Basalt							
A_{11} 0–2	10 YR 2/1 Bl*	6·0	17·02	65·9	34·7‡	47·6	17·7
A_1 2–5	10 YR 2/2 vd B	5·9	10·72	64·1	35·6‡	44·6	19·8
B 5–14	10 YR 2/2 vd B	5·8	7·74	61·9	41·5	40·2	18·3
C_1 14–32	10 YR 5/4 y B	5·6	1·90	90·0	53·6	34·2	12·2
C_2 32–37	10 YR 6/3 p B	5·8	0·33	60·8	46·2	7·9	..
Schist							
A_{11} 0–2	7·5 YR 2/0 B	5·2	17·22	13·3	45·2‡	38·1	16·7
A_1 2–4·5	10 YR 2/2 vd B	4·7	11·71	30·5	49·1‡	34·0	16·9
B 4·5–10	10 YR 2/2 vd B	4·5	8·93	17·8	59·9	26·7	13·4
C_1 10–16	10 YR 5/4 y B	4·6	1·12	17·6	68·2	26·2	5·6
C_2 16–36	10 YR 5/4 y B	4·8	0·40	44·0	75·5	22·3	2·2
Granite							
A_1 0–7	10 YR 2/2 vd B	5·7	4·32	41·2	64·5	24·2	11·3
B 7–18	10 YR 5/4 y B	5·6	0·56	54·4	69·9	29·0	1·1
C 18–24	10 YR 5/6 y B	5·3	0·54	36·6	78·7	14·5	6·8
Quartzite							
A_1 0–6	5 YR 3/1 vd G	4·5	10·23	15·3	44·9‡	34·3	20·8
B 6–22	7·5 YR 5/4 B	4·7	1·40	17·8	74·5	17·9	7·6
C 22–32	7·5 YR 5/6 s B	5·0	0·35	9·7	85·6	9·6	4·8
Shale							
A_1 0–5	5 YR 2/1 Bl	6·0	6·88	23·3	59·6	26·0	14·4
B 5–9	10 YR 5/4 y B	6·0	2·79	32·8	53·8	30·5	15·7
C_1 9–21	10 YR 5/4 y B	6·2	0·85	27·8	61·8	26·5	11·7
C_2 21–30	10 YR 5/3 B	8·2	0·32	69·2	57·0	33·9	9·1
Limestone							
A_1 0–6	7·5 YR 3/2 d B	7·7	7·96	47·1	64·4	25·1	10·5
B 6–18	7·5 YR 4/4 B	8·3	1·24	64·3	65·6	27·7	6·7
C 18–30	7·5 YR 5/4 B	8·4	0·62	65·4	66·1	26·7	7·2

* Bl—Black, B—Brown, G—grey, vd—very dark, d—dark, y—yellowish, p—pale, s—strong.
† Gravel computed as percentage of entire sample; sand, silt, and clay as percentage of the < 2 mm. fraction.
‡ Mechanical analyses by Retzer. All others, including organic carbon, by V. J. Kilmer.

decreases with depth. Soils from quartzite are the most acid. In most soils the pH range is remarkably small from the surface to the deepest layers.

The turf soils have high concentrations of organic carbon in the surface 5–7 in. Subdivision of the surface into A_{11} and A_1 showed still higher concentrations in the top 0–2-in. layer (A_{11}).

These soils are coarse-textured. Gravel makes up a high proportion

[1] A complete description of all laboratory methods and techniques is given in the thesis by John L. Retzer, 1950, 'Genesis and Morphology of Soils of Alpine Areas in the Rocky Mountains', on file and available on loan from the University of Wisconsin Library, Madison, Wisconsin.

of all horizons. The quantity of rocks is appreciable in the surface layers and increases with depth. Analysis of the < 2-mm. fraction shows that 16 of the 23 horizons contain more than 50 per cent. sand. Profiles from basalt contain the highest quantities of silt and clay while those from quartzite and granite are lowest in silt and clay.

The freeze-thaw cycle has not resulted in abnormal accumulations of a particular size fraction in any horizon. The same general pattern was found when the clays (< 2 μ) were further fractionated for the clay-mineral analysis. In this analysis the B horizon was selected for study. The results of the fractionation are shown in Table 3. These data show that very fine fractions occur in soils developed in the rigorous climate above 12,000 ft. in the Colorado Rockies.

TABLE 3

Fractionation of the Clays of Five Alpine Turf Soils

Rock type	*Depth*		*Fractions*		
	horizon	*inches*	2–0·2 μ (%)	0·2–0·08 μ (%)	< 0·08 μ (%)
Basalt . . .	B	5–14	11·2	5·7	2·1
Schist . . .	B	4·5–10	7·4	3·8	2·2
Granite . . .	B	7–18	2·2	0·7	0·6
Quartzite . . .	B	6–22	2·8	1·9	2·3
Shale . . .	B	5–9	8·8	3·5	2·1

Silts and clays are greatest in the surface horizon on all profiles. It has been suggested that this is the result of wind deposition, but on fractionation into five classes (2–1, 1–0·5, 0·5–0·25, 0·25–0·1, and 0·1–0·05 mm.) each soil showed the same class-size distribution pattern for all horizons. In all instances there was some increase in the percentage of the finer grades (0·25–0·1 and 0·1–0·05 mm.) in the lower horizons. This does not prove that wind-deposited materials are not present on the surface; their importance as the only source of the silt and clay is questionable. The concentration of silt and clay in the surface soil (A_{11} and A_1) appears to arise in part from genetic and weathering processes. In this zone, the greatest biological activity must occur, resulting in the greatest release of CO_2 and organic acids. The surface soil must be warmer, an important factor in a region where heat is at a premium.

Bulk density was determined for the combined A_{11} and A_1 horizons of six soils. The values ranged from 0·94 to 1·14 and the mean was 1·02, reflecting good structural arrangement and especially the large quantity of organic materials present.

The exchangeable cations of seven profiles are shown in Table 4. Similar distribution patterns occur in all soils. Bases are present in largest quantities in the surface layers and decrease with depth in the profile. Sodium, when present, occurs only in small quantities and usually only in deeper horizons. Phosphorus is erratically distributed but tends to increase with increasing depth, while exchangeable cations decrease.

TABLE 4

Exchangeable Cations and Available Phosphorus in Seven Alpine Turf Soils from Different Parent Rocks

Soil and horizons*	Total base ex. capacity (m.e.†)	Exchangeable cations					Available P (lb./acre)
		Ca (m.e.)	Mg (m.e.)	K (m.e.)	Na (m.e.)	H (m.e.)	
Basalt							
A_{11}	58·0	44·16	7·52	0·90	0	5·42	40
A_1	45·2	37·75	5·84	0·60	0	1·01	30
B	35·2	30·34	4·44	0·19	0	0·23	40
C_1	15·7	10·60	2·00	0·10	0·15	2·85	30
C_2	8·4	6·14	1·22	0·18	0·06	0·80	200+
Schist							
A_{11}	35·5	23·56	3·90	0·61	0	7·43	30
A_1	21·4	9·42	1·90	0·19	0	9·89	20
B	15·2	4·22	0·72	0·08	0·01	10·17	10
C_1	6·9	0·38	0·02	0·01	0·01	6·48	30
C_2	3·6	1·94	0·14	0·04	0·01	1·47	40
Granite							
A_1	24·2	16·59	2·20	0·18	0·01	5·28	10
B	4·5	2·82	0	0·03	0·01	1·64	40
C	8·1	2·42	0	0·05	0·03	5·60	35
Quartzite							
A_1	29·6	8·08	0·80	0·37	0·02	20·33	20
B	6·6	6·13	0	0·03	0	0·44	30
C	3·0	2·19	0	0·01	0	0·80	60
Shale							
A_1	39·4	22·97	4·86	0·53	0	11·03	20
B	17·3	12·29	2·62	0·23	0·01	2·15	5
C_1	10·4	7·31	2·82	0·07	0·01	0·19	10
C_2	26·3	14·78	11·44	0·05	0	0	30
Limestone							
A_1	..	..	..	0·19	..	0	25
B	..	..	..	0·03	..	0	40
C	..	..	..	0·04	..	0	180
Andesite							
A_{11}	20·4	13·79	2·96	0·45	0	3·20	70
A_1	17·2	10·15	2·38	0·32	0·03	4·32	40
B	15·6	7·04	1·68	0·08	0·08	6·72	30
C	8·1	5·08	1·08	0·05	0·03	1·86	60

* Soil developed from the rocks shown. Horizon depths same as shown in Table 1.
† Milliequivalents per 100 gm. of oven-dry soil.

The degree of rock alteration that has occurred in the turf soils was studied. The B horizons of soils from basalt, schist, granite, quartzite, and shale were analysed. The rocks of the first three soils are undergoing their first weathering cycle; shale and quartzite are deposits from previous weathering cycles.

The following fractions were analysed by X-ray diffraction: 5–2 μ, 2–0·2 μ, 0·2–0·08 μ, and $< 0{\cdot}08$ μ. Kaolinite was determined by heating

the clay on the glass slide to 520° C. for 30 min. Pre- and post-heating diffraction patterns were compared, and the portion of the 3·5-Å and 7·2-Å lines which disappeared on heating to 520° C. were considered

TABLE 5

*Minerals Identified by X-Ray Diffraction and Estimated Quantity of Each from One Horizon of Five Alpine Turf Soils from Different Parent Rocks**

Profile no. and parent material	*Horizon and depths (inches)*	*Minerals identified and estimated quantity of each in % for each fraction*			
		(5–2 %)	(2–0·2 %)	(0·2–0·08 %)	(< 0·08 %)
23	B	Q† 15	Q 10	Q 15	Q 15
Basalt	5–14	Ill 30	Ill 20	Ill 20	Ill 25
		Orth 30	Orth 10	ChKl 10	X 20
		Ch 20	Kl(Ch?) 20	X 25	Kl 10
		Mt 5	Mt–Vr 40	Mt–Vr 30	Mt 30
26	B	Q 25	Q 20	Q 15	Q 15
Mica	4·5–10	Ill 40	Ill 30	Mt–Vr 40	Ch 20
Schist		Orth 20	Orth 15	X 30	X 25
		Kl(Ch?) 15	Kl(Ch?) 35	Kl 15	Mt–Vr 25
		..	..	..	Ill 15
39	B	Q 15	Q 15	Q 15	Q 15
Biotite	7–18	Ill 45	Ill 45	Ill 30	Ill 25
Granite		Orth 15	Orth 15	Albite 5	Ch 10
		Kl 20	Kl 20	Ch 15	Kl 10
		Mt–Vr 5	Mt–Vr 5	Kl 15	Mt–Vr 25
		..	..	Mt–Vr 20	X 15
29	B	Q 20	Q 20	Q 15	Q 15
Quartzite	6–22	Ill 30	Ill 30	Ill 40	Ch 30
		Orth 10	Orth 10	Ch 25	Mt–Vr 25
		Ch 15	Ch 15	Kl 20	Ill 10
		Kl 20	Kl 25	..	X 20
43	B	Q 20	Q 40	Q 25	Q 10
Shale	5–9	Ill 30	Ill 25	Ill 30	Ill 15
		Orth 10	Orth 10	Orth 5	Orth 5
		Ch 15	Kl(Ch?) 25	Albite 5	Mt–Vr 30
		..	..	Kl(Ch?) 40	X 20
		Kl 25	..	..	Chl 10
		..	..	..	Kl 10

* Assistance in mineral identification was given by Professor M. L. Jackson, who also estimated the relative quantities of each mineral present.

† Symbols used: Ch = Chlorite; Ill = Illite including all micas; Kl = Kaolinite; Mt = Montmorillonite; Orth = Orthoclase; Q = Quartz; X = Hydrous Clay intermediates; Vr = Vermiculite.

to represent kaolinite and the portion of the 14-Å line which shifted to 10 Å on heating was attributed to vermiculite. The remaining 7-Å and 14-Å lines were considered to represent chlorite. When no part of the 7-Å and 14-Å lines remained, both vermiculite and kaolinite were considered to be present and chlorite absent. The montmorillonite-vermiculite complex was considered a 2:1 layer silicate giving diffraction

maxima between 14 Å and 18 Å but indistinctly differentiated and probably involving interstratification. A group of hydrous-clay intermediates with indistinct basal diffraction diffuse between 11 Å and 14 Å was also present.

Results of the mineral analyses in Table 5 show kaolinite, montmorillonite-vermiculite, and chlorite in most fractions of all soils, indicating that chemical alteration and clay formation are reasonably well advanced. Quantitative values in percent. are estimates only and are subject to correction with more research. It is significant that kaolinite, often considered well along in the weathering sequence (Jackson *et al.*, 1948), is present in these soils. The mineralogical analyses suggest some mixing of the soil material. For example, clays in the quartzite-derived soil suggest admixture from other rock sources.

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PROFILE DEVELOPMENT IN THE SAND DUNES OF CULBIN FOREST, MORAYSHIRE

II. CHEMICAL PROPERTIES

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A PREVIOUS communication (Wright, 1955) has traced some physical changes in the Culbin sand dunes under tree crops of different species and age classes. The present study deals with changes in the distribution of major nutrients in the profile on the same sites, brought about by their uptake by the crop and subsequent return as litter.

Collection and Preparation of Samples

Samples were taken from each of the plots previously described, namely, naturally fixed *Ammophila* dune (plot A), 12-year Corsican pine (plot B), 22-year Corsican pine (plot C), 45-year Corsican pine (plot D), 80-year Scots pine (plot E), 40-year birch (plot F), and recently planted 'thatched' dune (plot G). Since both thatched and naturally fixed dune have undergone a certain amount of weathering since their stabilization, samples of sand unaffected by pedogenic processes were also taken from an eighth plot (H), laid out on the flat summit of a still mobile dune. The final samples for analysis were reduced in a Jones sample splitter from a composite field sample.

Litter from the plots bearing trees was collected in metre-square wooden trays at bimonthly intervals; three trays were spaced randomly in each plot, and moved after each collection. The weight of oven-dry litter collected over the whole of 1952 is shown in Table 1. The

TABLE 1

Collection of Leaf Litter

	Dry Weight (Oven-dried at 80° C.) of litter collected (g).											
	Jan.–Feb.				*Mar.–Apr.*				*May–June*			
Plot	*Tray 1*	*2*	*3*	*Average*	*Tray 1*	*2*	*3*	*Average*	*Tray 1*	*2*	*3*	*Average*
B	1·8	2·4	2·3	2·2	0·5	0·5	0·1	0·4	5·0	6·3	8·7	6·7
C	3·2	3·6	3·3	3·4	0·7	0·9	1·0	0·9	7·9	7·1	15·0	10·0
D	7·0	4·9	6·2	6·0	1·6	1·6	1·0	1·4	3·1	3·0	3·3	3·1
E	2·7	2·3	3·9	2·9	2·1	1·3	2·6	2·0	4·1	11·0	8·5	7·9
F	6·0	11·1	1·0	6·0	2·1	3·1	2·1	2·4	3·6	7·6	8·1	6·4
	July–Aug.				*Sept.–Oct.*				*Nov.–Dec.*			
Plot	*Tray 1*	*2*	*3*	*Average*	*Tray 1*	*2*	*3*	*Average*	*Tray 1*	*2*	*3*	*Average*
B	13·9	14·3	11·1	12·8	19·6	26·7	25·4	23·9	6·8	22·2	33·4	20·8
C	21·1	15·0	20·1	19·1	24·0	17·7	46·4	29·4	42·4	39·8	38·4	40·2
D	6·0	14·5	22·6	14·4	100·6	101·5	149·5	117·1	31·6	26·1	27·7	28·5
E	5·6	5·8	3·0	4·6	7·9	6·2	8·4	7·5	2·1	4·9	10·7	5·9
F	3·7	6·4	2·9	4·3	21·3	20·0	19·4	20·2	7·0	2·7	4·7	4·8

relatively large amounts of pine litter falling in the autumn, particularly in the 12-year and 45-year Corsican pine plots, agree with the findings of Chandler (1943) that although conifers shed their needles to some extent continuously, the greatest amount is shed in the autumn. The high figure for birch in the May–June period was composed principally of flower debris.

Methods of Analysis

Available cations and phosphate were leached from the sand samples with 2·5 per cent. acetic acid. Potassium, magnesium, and sodium in the leachate were determined spectrographically (Mitchell, 1948). Calcium was determined by precipitation as the oxalate followed by titration with potassium permanganate, since the level of available calcium in the sand was too low for spectrographic determination. Available phosphate was determined colorimetrically with sodium molybdate (Williams and Stewart, 1941), and total phosphate by sodium carbonate fusion followed by a similar colorimetric method (Muir, 1952).

Total calcium, magnesium, potassium, and sodium in the litter was determined by spectrographic analysis of 0·1 N HCl extracts of the ashed material. Total phosphate was determined colorimetrically after wet digestion with nitric and perchloric acids, and total nitrogen by the semi-micro Kjeldahl method of Markham (1942).

Results

(*a*) *The effect of ground cover on the nutrient content of the soil*

The incorporation of organic matter into the upper layers of the profiles developed under the older trees causes a reduction in their apparent density, and nutrient content under these conditions is best expressed on a volume basis. The apparent density of the soil in the sample plots, determined with a 3-in. diameter sampling tube, is given in Table 2; this shows good agreement between replicates in layers unaffected by organic matter but a greater spread of readings in the humose layers of plots C, D, E, and F.

TABLE 2

Apparent Density of the Soil in the Sample Plots (g./litre)

Depth (in.)	*Plot A*	*B*	*C*	*D*	*E*	*F*	*G*	*H*
0 .	1,377±9	1,213±23	823±20	670±23	590±17	1,020±17	1,253±9	1,223±9
6 .	1,380±6	1,333±9	1,340±11	1,280±17	1,270±17	1,320±6	1,380±2	1,370±6
12 .	1,323±5	1,303±14	1,383±14	1,320±6	1,260±11	1,253±3	1,420±23	1,380±2
24 .	1,340±6	1,300±11	1,250±17	1,373±9	1,363±9	1,240±23	1,400±2	1,140±6
36 .	1,350±2	1,310±17	1,283±9	1,340±20	1,313±9	1,400±6	1,370±6	1,373±3
48 .	1,317±3	1,310±11	1,253±3	1,307±9	1,353±9	1,333±9	1,343±3	1,363±3
86 .	1,323±3	1,310±11	1,253±3	1,313±3	1,300±6	1,310±2	1,320±2	1,340±2

The results of the chemical analyses are shown graphically in Fig. 1. They illustrate the three main processes taking place in the sand; removal by leaching, removal by the crop, and replenishment of the surface horizons from the litter. Thus in the case of calcium, the amount

in the unweathered dune (plot H) varies between 65 and 85 mg. CaO per litre at all depths down to 5 ft., but in a fixed dune exposed to leaching and some removal by vegetation (plot A), the value falls to 40–45 mg. in the top 6 in., and 50–55 mg. in the remainder of the profile. Thatching (plot G) has resulted in an increase in available calcium in the top 6 in. Before the closure of canopy (plot B) young trees remove large amounts of calcium from the top foot of soil, in which lie the majority of the feeding roots; older trees (plots C–F) remove calcium from the lower horizons, but litter fall results in large increases at the surface. In plot D the 45-year Corsican pine causes a reduction in calcium throughout the profile.

Potassium shows similar trends, leaching reducing K_2O content from 15–25 mg. per litre to about 10–15 mg. Thatch and the older trees enrich the surface soil, with the exception of birch; there is no sign of removal by trees below the 3-ft. level.

There is little improvement in the magnesium content of the surface soil except in the oldest trees (plots D, E, and F). The content is particularly low under birch down to 4 ft.

Sodium is an example of an element in plentiful supply in the sand, which is not taken up in such large amounts by the trees, and is therefore subject mainly to leaching.

The available phosphate levels follow the same trends as calcium and potassium; total phosphate is reduced in the planted plots at the surface, and at depths of 1–3 ft.

(*b*) *Influence of grain size on the nutrient content of the soil*

A composite sample was made up from the humus-free horizons of all the plots, and separated into five size fractions by dry sieving. Chemical analysis of these fractions gave the results shown in Table 3; calcium

TABLE 3

Influence of Grain Size on the Nutrient Content of the Soil

Grain size (mm.)	*Available nutrients (mg./100 g. sand)*				*Total phosphate*
	K_2O	Na_2O	MgO	P_2O_5	P_2O_5
0·5–0·295 . .	1·02	1·84	0·70	0·200	18·1
0·295–0·251 . .	1·03	1·73	0·73	0·168	27·2
0·251–0·211 . .	1·01	1·86	0·67	0·256	27·9
0·152–0·104 . .	1·05	1·96	0·71	0·608	43·8
< 0·104 . .	1·08	1·95	0·74	0·895	56·4

determinations had to be omitted owing to lack of material. While there is little increase of available bases with decreasing grain size, both available and total phosphate increase very markedly in the two smallest fractions. This can be explained on mineralogical grounds; sodium and potassium in the Culbin material are chiefly derived from the felspars which constitute the 'light' mineral fraction (S.G. less than 2·87),

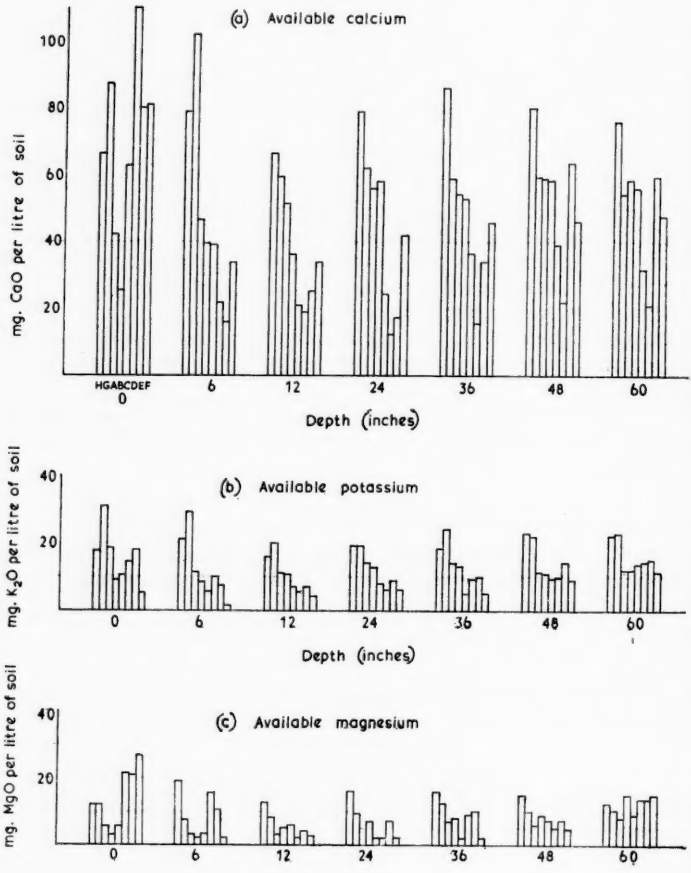
(a) Available calcium
mg. CaO per litre of soil
100
80
60
40
20
HGABCDEF
0
6
12
24
36
48
60
Depth (inches)
(b) Available potassium
mg. K_2O per litre of soil
40
20
0
6
12
24
36
48
60
Depth (inches)
(c) Available magnesium
mg. MgO per litre of soil
40
20
0
6
12
24
36
48
60

FIG. 1

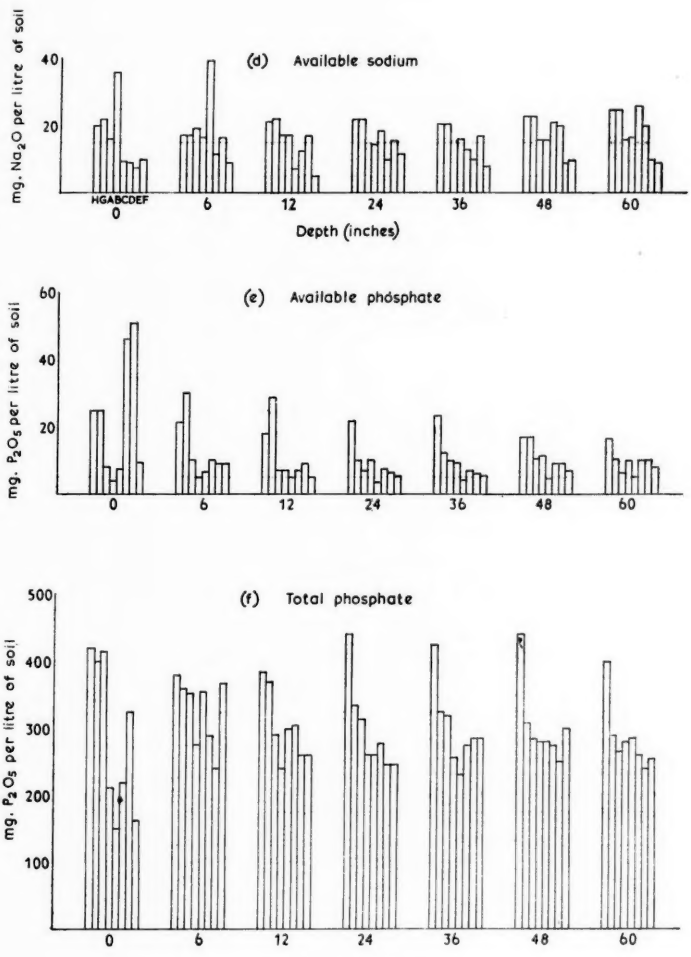
(d) Available sodium
mg. Na_2O per litre of soil
40
20
HGABCDEF
0
6
12
24
36
48
60
Depth (inches)
(e) Available phósphate
mg. P_2O_5 per litre of soil
60
40
20
0
6
12
24
36
48
60
(f) Total phosphate
mg. P_2O_5 per litre of soil
500
400
300
200
100
0
6
12
24
36
48
60

FIG. 1 (*cont.*)

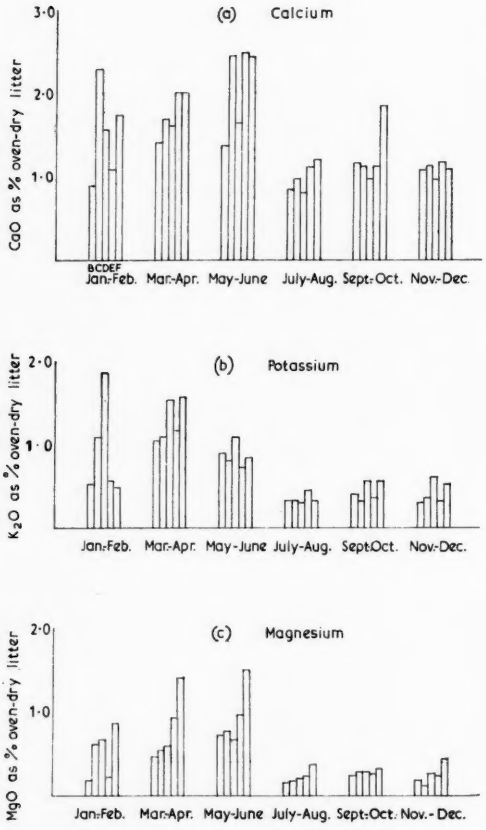
(a) Calcium
CaO as % oven-dry litter
3·0
2·0
1·0
BCDEF
Jan:-Feb.
Mar:-Apr.
May-June
July-Aug.
Sept:-Oct.
Nov-Dec.
(b) Potassium
K_2O as % oven-dry litter
2·0
1·0
Jan:-Feb.
Mar:-Apr.
May-June
July-Aug.
Sept:Oct.
Nov-Dec.
(c) Magnesium
MgO as % oven-dry litter
2·0
1·0
Jan:-Feb.
Mar:-Apr.
May-June
July-Aug.
Sept:-Oct.
Nov.-Dec.

FIG. 2

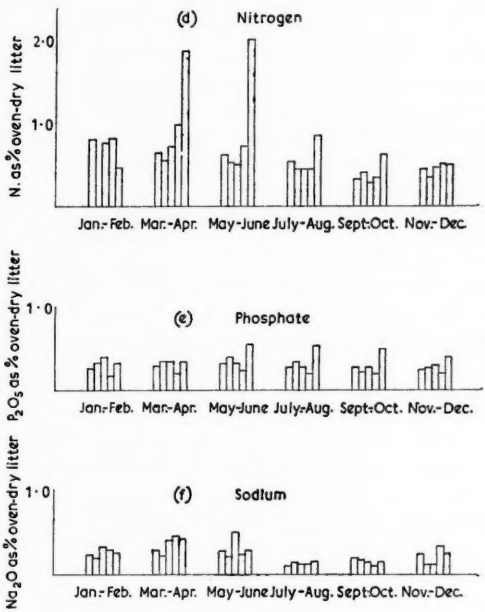
(d) Nitrogen
N. as % oven-dry litter
2·0
1·0
Jan.-Feb. Mar.-Apr. May-June July-Aug. Sept.-Oct. Nov.-Dec.
(e) Phosphate
P_2O_5 as % oven-dry litter
1·0
Jan.-Feb. Mar.-Apr. May-June July-Aug. Sept.-Oct. Nov.-Dec.
(f) Sodium
Na_2O as % oven-dry litter
1·0
Jan.-Feb. Mar.-Apr. May-June July-Aug. Sept.-Oct. Nov.-Dec.

FIG. 2 (*cont.*)

whereas phosphate is derived from apatite, a heavy mineral which, due to the efficient wind sorting, is found almost exclusively in the smallest size classes.

(*c*) *The nutrient content of the litter*

There is considerable evidence to show that nutrient content is more dependent on species, both hardwoods and conifers, than on the nutrient status of the site, provided that this lies within certain broad limits. Metz (1952) finds no correlation between soil type and the nutrient status of the litter of Shortleaf pine (*P. echinata*) and Loblolly pine (*P. taeda*); Chandler (1941) finds that for deciduous species in forests in New York State, with high nutrient requirements relative to conifers, there is no correlation between the calcium status of the foliage and that of the soil except in the most acid sites (pH less than 4·0), and McVickar (1949) also finds no significant foliage difference except between the worst and the best of his sites. Aaltonen (1950), comparing the nutrient content of foliage of Scots pine, Norway spruce, and birch, grown on different Cajander forest site types in Finland, finds that only birch reacts strongly to improvement in site type, the effect being most marked in the calcium and nitrogen content.

The nutrient content of tree litter has also been found to vary appreciably throughout the year. Alway, Maki, and Methley (1934) report that in both hardwoods and conifers the calcium content of the litter increases considerably (50 per cent.) from June to October, magnesium increases slightly, and nitrogen and phosphate decrease by about 30 per cent. The decrease in nitrogen is also noted by McHargue and Roy (1932). McVickar (1949) observes a fall in potassium as well as phosphate and nitrogen, and confirms that calcium increases, magnesium remaining roughly constant throughout the year.

The results of the present study are given in Fig. 2.

These show an abrupt fall in the level of calcium, potassium, sodium, and magnesium in the July–August period, as well as a slight, steady decrease in nitrogen and phosphate throughout the year.

Discussion

Stabilization and subsequent growth of vegetation on the sand has had a very marked effect on its chemical composition, and analysis reveals redistribution of nutrients on a considerably greater scale than is suggested by inspection of profiles in the field. Leaching of readily soluble nutrients becomes appreciable within a short time of stabilization, and occurs in areas bearing only the sparsest vegetation. The planting of trees superimposes on this almost purely climatic leaching a second movement, that of removal of nutrients by the vegetation. This results in a marked decrease in nutrient content in the lower horizons in which the main mass of the rooting system lies, and an increase at the surface due to the incorporation of organic matter. In the younger age classes (plot B) the as yet shallow rooting system makes such demands on the surface soil that removal exceeds return in spite of a relatively large leaf

fall. Plot C shows, however, that after 22 years the closure of canopy and increased litter fall has restored the nutrient status of the surface soil, although the depth at which removal is taking place has greatly increased. In plot D rooting depth has still further increased, but enrichment of the surface layers has increased proportionally to a greater extent, resulting in an overall improvement in nutrient status as compared with the two plots of younger trees. It appears, therefore, that up to about 15–20 years (or roughly until the complete closure of canopy) removal of nutrients is most rapid, and thereafter the downward percolation of nutrients from the litter tends to restore the balance. A net decrease is always evident due to the large amount of nutrients temporarily immobilized in the crop.

The present study shows little difference in the nutrient uptake of Scots and Corsican pines, although the active rooting depth of the Corsican appears to be greater. Levels of available phosphate, potassium, and magnesium are particularly low in the birch plot. This is probably due to the open nature of the stand and the poor growth resulting from too dry a site, giving a small litter fall and strong growth of mosses on the soil surface.

The general level of the total phosphate content of the sand is extremely low. In this connexion it is interesting to note that Stoate (1950) considers that the following minimum values for total phosphate are necessary for satisfactory growth of *Pinus pinaster* and *P. radiata* on the Western Australian sand dunes:

Pinus pinaster 150 p.p.m.; *P. radiata* 300–400 p.p.m.

Since it is the phosphate, both total and available, which increases so markedly with decreasing sand-grain size, the importance of the finest sand fractions to the nutrient status of the soil will be apparent.

The seasonal variations in nutrient content, in contrast to the experience of other workers, show a sharp drop in the nutrient content of the litter of all species collected in the July–August period except in the case of phosphate, which declines steadily throughout the growing season, and nitrogen, which shows a minimum value in the September–October period. The drop in calcium, magnesium, and potassium is particularly marked. The moisture studies previously reported have shown that drying of the soil in the rooting zone reaches a maximum towards the end of May, and thereafter remains low for the remainder of the growing season. Allowing for the time taken for the deposition of a litter of needles growing during this period, it is possible that the moisture content of the soil under all the tree crops studied is reduced by transpiration during the growing season to such a low level that it seriously interferes with nutrient uptake, which does not recover during the remainder of the year. That the uptake of sodium, an element which is not a major nutrient of trees, and which is in abundant supply in the Culbin soil, is similarly affected, shows that the decrease is not caused by simple deficiency. Further work on this question is in progress.

Acknowledgements

The whole investigation was supervised by the late Dr. G. K. Fraser, of the Department of Soil Organic Matter, The Macaulay Institute. I am also indebted to Dr. R. L. Mitchell who arranged for the spectrochemical analysis of the soil and plant material, and Mr. R. H. E. Inkson who performed the statistical analyses. The work was carried out under a grant from the Forestry Commission, and of the Commission staff I am particularly grateful to Mr. F. W. A. Oliver, Conservator, Scotland East Conservancy, Mr. J. A. M. Kennedy, District Officer, and Mr. W. G. Milne, Head Forester at Culbin, who made available sample plot measurements and rainfall records.

Summary

Chemical analysis of the soil from a range of sites at Culbin Forest, Morayshire, has revealed considerable redistribution of the major nutrients taking place after dune fixation, and has distinguished between the downward movement due to leaching and the circulation initiated by the tree crop. Analysis of the litter has shown abnormal seasonal variations in its chemical content.

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THE FORMATION OF DARK-COLOURED CLAY-ORGANIC COMPLEXES IN BLACK SOILS

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BLACK colour in soils is often associated with conditions of high fertility and has therefore attracted considerable attention. But it has been studied more from the standpoint of the colour-producing constituents than of the principles of colour production. It is generally held that black colour results when a soil is formed under conditions of restricted drainage and in neutral or alkaline conditions of environment (Hosking, 1940; Nagelschmidt, Desai, and Muir, 1940; Mukerji and Agarwal, 1943; Hallsworth and associates, 1952, &c.). The few scattered studies of the colour principle (Leather, 1898; Annett, 1910; Harrison and Ramaswami Sivan, 1911–12; Schokalsky, 1932, &c.) attribute the colour to the presence in the soils in their finer fractions of black-coloured minerals such as titaniferous iron oxides or to coloured organic iron complexes. Conclusive evidence of the presence of the responsible mineral is in no case available.

Working on some typical black soils of India, Singh (1954*b*) has shown that the basic black colour resides mainly in their clay-humus complexes and is destroyed by oxidation of the organic component by H_2O_2. Some insight into the nature of the colour-producing complex has been obtained from the nature of the products of peroxidation. These were found to show a higher C:N ratio than the organic matter component of the black soil clay. Treatment of the coloured complex with strong mineral acids results in a preferential loss of its nitrogen with little or no destruction of the colour principles (Singh, 1954*a*). It would appear that the black colour in these soils is a contribution of the more carbonaceous constituents of the organic component of the clay-humus complex. It was felt that studies of colour formation under easily reproducible conditions in the laboratory might lead to better definition of the colour principle. With this object in view, clay-organic matter complexes were synthesized from typical but decolorized clays and organic complexes obtained under well-defined conditions.

Materials and methods

Table 1 furnishes a description of the soils used in these studies. A red soil and samples of pure clay minerals were also included for comparison.

Preparation of peroxidized clays

The soils were first dispersed by 'Calgon' and the clay separated by repeated sedimentation. The separated clays were completely peroxidized to decolorize them. They were then treated with 94 per cent.

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TABLE 1
Soil Samples

Sample	*Depth in inches*	*Locality*	*Characteristics*
Rendzina . .	0–7	Ivinghoe Hills (Buckinghamshire) ¼ mile south of Beacon, England.	Dark greyish-brown humose loam; just moist; crumb structure very friable; occasional angular chalk fragments and small calcareous particles.
Chernozem .	0–15·5	A deep chernozem from Kharkov (Russia)	Dark grey or dark brownish in colour; friable and granular.
Red . . .	12–24	Kullioor, Coimbatore, India.	Dark red; loose and friable; presence of quartz fragments.
Black cotton soil .	12–24	G. N. Palayam, Coimbatore, India.	Very dark grey; loosely compact and granular.

alcohol twice or thrice and then finally with absolute alcohol to remove most of the remaining moisture. The alcohol-treated clays were dried at 30–40° C. and then ground to a fine powder. Other clay minerals used were also treated similarly and dried.

Organic complex

It is well known that a soluble form of humus is not obtainable without the probable alteration of its original chemical nature. Hence it was thought desirable to use a decomposition product of plant material which was sufficiently active to be capable of interaction with clay. Preliminary experiments showed that a water extract of anaerobically fermented grass was capable of reacting and forming dark-coloured complexes with certain clays and was chosen for these studies (Bloomfield, 1951).

Preparation of the extract

Grass from one of the Rothamsted fields was dried, ground in a Raymond mill, and passed through a 60-mesh sieve. Carbon, nitrogen, and iron contents of this powder were 39·8, 2·8, and 0·95 per cent. respectively. The fermentation was carried out under anaerobic conditions in an atmosphere of nitrogen following a method similar to that of Bloomfield (1951). The ratio of grass to water was 1:10 by weight. Some of the fermentations were carried out in the presence of ferric hydroxide in which case the amount of moist hydroxide was about one-fourth the amount of grass. After a few days' fermentation the solid iron hydroxide was no longer visible and was closely associated with the organic matter of the fermenting extract.

A period of at least 4 weeks was allowed for the fermentation. Samples of the fermented extract were expelled from the reaction vessels by nitrogen, cloth filters being used for keeping back the unfermented

matter of the grass. The extracts were centrifuged for half an hour at 1,000 r.p.m. and the clear supernatant liquids used for interactions with the clays.

The extract from grass fermented without iron is briefly referred to as the 'G-extract', and the one with iron as the 'FeG-extract'.

Method of interaction

The reactions were carried out in centrifuge bottles fitted with rubber bungs. One gramme of clay sample and 100 ml. extract, in general, were taken in the bottles which were then shaken end-over-end for 3 or 4 hours daily. The extracts, when freshly prepared, were light greenish-yellow in colour and gradually darkened on exposure to the atmosphere. Therefore, a small amount of air was allowed into each bottle every day and the reaction allowed to proceed for a period of 15 days. The pH of the clay samples and extract was in all cases about 5·0, and when necessary was adjusted to the required value by addition of acid or alkali.

Determinations

The final products were centrifuged and the supernatant liquids transferred to measuring flasks. The residues were washed with water by centrifugation, the washings being added to the flasks and made up to volume. Carbon and nitrogen were determined on the clay-organic complexes, and the other inorganic elements were determined on aliquots of the centrifugate.

Results

Colour of the interaction products

In Table 2 the colour of the clays before and after reaction is given, the colour being expressed in terms of Munsell standards. As will be seen, after reacting with the extract the clays of the rendzina, chernozem, and the black soils acquired characteristic dark shades as also did the pure minerals bentonite and illite. Kaolinite, on the other hand, did not become dark or grey, and the red soil clay, rich in this latter clay mineral, showed a similar behaviour. It will be noted from Tables 2 and 3 that only those clays containing predominantly montmorillonite became very dark. The nature of the clay mineral is, therefore, an important factor in the formation of the dark colour. The amounts of organic matter sorbed, as measured by the carbon content, do not appear to be strictly related to colour production, though in general, darker shades are accompanied by higher degrees of sorption, kaolinite sorbing only 7·2 mg. of carbon per gramme of clay, while bentonite and the black soil clays sorb 32·0 and 36·5 mg. respectively. Further, the red soil clay shows a high sorption but little colour production. A parallel between these two related features in natural soil occurrences is evident —the red soil possesses no intrinsic dark shade in spite of high organic matter content.

The reaction products of the FeG-extract showed similar trends, though in every one of these cases the resulting colours on analysis were

TABLE 2

Colours of the Clays before and after Interactions

Sample	*Unperoxidized*	*Peroxidized*	*Type of extract*	*The peroxidized clay after interaction*
Kaolinite (< 0·5 μ) .	White (10 YR 9/1; same when moist).	..	G	White (10 YR 9/1; 10 YR 7/1, light grey moist).
Illite . .	Grey (10 YR 6/1; 10 YR 4/1, dark grey moist).	Light olive (5 Y 6/2; 5 Y 6/1, grey moist).	G	Greyish-brown (10 YR 5/2; 10 YR 4/1, dark grey moist).
Rendzina clay .	Black (5 YR 2/1; 10 YR 2/1, black moist).	Light brown-grey (2·5 Y 6/2; same when moist).	G	Grey (10 YR 5/1; 10 YR 2/2, very dark brown moist).
Chernozem clay .	Very dark grey (2·5 YR 3/0; 2·5 YR 2/0, black moist).	Dark brown (10 YR 4/3; 10 YR 3/3, dark brown moist).	G	Very dark greyish-brown (10 YR 3/2; 10 YR 2/2, very dark brown moist).
Bentonite . .	Light grey (5 Y 7/1; 5 Y 6/1, grey moist).	..	G	Dark greyish-brown (2·5 Y 4/2; 2·5 Y 3/2, very dark greyish brown moist).
,, . .	Light grey (5 Y 7/1; 5 Y 6/1, grey moist).	..	Fe G	Yellowish-brown (10 YR 5/4; 10 YR 3/3, dark brown moist).
Red soil clay .	Dark reddish-brown (2·5 YR 3/4; same when moist).	Dark red (10 R 3/6; same when moist).	G	Dark reddish-brown (2·5 YR 3/4; same when moist).
,, .	Dark reddish-brown (2·5 YR 3/4; same when moist).	Dark red (10 R 3/6; same when moist).	Fe G	Reddish-brown (5 YR 4/3; 5 YR 3/3, dark reddish-brown moist).
Black soil clay .	Very dark grey (10 YR 3/1; same when moist).	Light brown-grey (2·5 Y 6/2; same when moist).	G	Very dark grey (10 YR 3/1; 10 YR 2/1, black moist).
,, .	Very dark grey (10 YR 3/1; same when moist).	Light brown-grey (2·5 Y 6/2; same when moist).	Fe G	Greyish-brown (10 YR 5/2; 10 YR 3/2, very dark greyish-brown moist).

G stands for extract of the grass fermented alone.
Fe G ,, ,, ,, ,, ,, in presence of iron.

TABLE 3

Clay Minerals present in the Soils

Sample	*Clay minerals*
Rendzina . . .	Consists mainly of calcite and montmorillonoid. Kaolin can also be detected. There is also probably a trace of quartz.
Chernozem . . .	Kaolin, illite, montmorillonoid (poorly crystallized), a little degrading illite, traces of calcite, quartz, and probably a trace of felspar.
Red soil . . .	Probably a mixture of coarse clay and fine clay of very different particle size. The fine clay is mainly a kaolin type mineral, perhaps metahalloysite, and haematite. The coarse clay contains illite, vermiculite, probably a little kaolin, traces of quartz and felspar.
Black soil (Regur) .	Montmorillonoid dominant, little kaolin, traces of felspar and quartz.

found to have a higher concentration of red, due obviously to the greater iron content of the extracts used. The amounts sorbed were not very different from the G-extract. Other experiments showed that the amount of the dark pigment formed under waterlogged conditions in presence of iron was lower than that formed in its absence (Singh, 1954*a*). The FeG-extract in the above reactions might also have contained a low amount of the dark pigment. Evidence for this was found

when equal volumes of G- and FeG-extracts were treated with an alkali solution. The intensity of the colour produced by the G-extract was about four times greater than that from the FeG-extract. The explanation of this difference lies most probably in the fact that in the preparation of the FeG-extract reduction of the ferric iron (Bloomfield, 1951) necessarily involved oxidation of some of the organic constituents.

The organic matter sorbed

The carbon and nitrogen contents of the sorbed organic matter of the products and their ratios are given in Table 4. The ratios differ little,

TABLE 4

Amount and C:N *Ratio of the Organic Matter sorbed by 1 g. of the* Ca-*clay from 100 ml.* G-*extract*

Sample	*Nature of the extract*	*mg.*C	*mg.*N	C/N	*Colour of the treated clay*
Kaolinite . .	G	7·2	2·0	3·6	White
Illite . . .	G	25·2	4·8	5·25	Greyish-brown
Rendzina clay .	G	34·92	6·5	5·37	Grey
Chernozem clay .	G	21·66	4·3	5·04	Very dark greyish-brown
Bentonite . .	G	32·0	5·5	5·82	Dark greyish-brown
„ . .	Fe G	36·8	8·1	4·54	Yellowish-brown
Red soil clay .	G	26·1	4·3	6·07	Dark reddish-brown
„ „ „ .	Fe G	25·0	4·6	5·43	Reddish-brown
Black soil clay .	G	36·5	6·6	5·53	Very dark grey
„ „ „ .	Fe G	38·9	8·8	4·42	Greyish-brown

G Extract of the grass fermented alone.
Fe G „ „ „ „ in presence of iron.

the values for the pure minerals as well as the clays lying between 5 and 6. Kaolinite, however, gave a product which had a C:N ratio of 3·6.* In general the value of the ratio is low compared with the normal value of 10 for the organic matter of most black-coloured soils. It appears that nitrogenous components of the fermented extract are absorbed preferentially. Further, in several of the later experiments in which the conditions of the interaction were varied in respect of their reaction and the nature of the reacting clay component, the C:N ratios of the sorbed organic matter remained the same. It is clear that the nature of the organic matter sorbed is very similar in all cases and thus of the whole reactable complexes as such.

Role of inorganic constituents of the extract

The black colour of soils has been attributed by many workers to the base saturated nature of the humus (Van der Merwe, 1935; Desai, 1942;

* Similar low values reported in the earlier paper by Dr. Singh (1954*b*) led to a suggestion that they might be due to sorbed ammonium. A careful repeat by C. L. Bascombe of some of the previous determinations after peroxidation, with and without treatment with $CaCl_2$, gave results almost identical to those obtained by Dr. Singh. It appears, however, that with some soils adsorbed ammonium formed on peroxidation may vitiate the C:N ratios. (A. Muir.)

Hallsworth *et al.*, 1952). The amounts of the inorganic constituents sorbed by the peroxidized clay should therefore be of interest, and these were estimated in the extracts before and after reactions. The values are given in Table 5.

TABLE 5

Cations sorbed by the Ca-*clay in μg./g. from 100 ml.* G-*extract*

Sample	Fe	Al	Si	Mn	Mg	Na	K
Kaolinite . .	475	−1,415	−1,120	5	425	35	500
Illite . .	1,175	−1,805	−1,120	70	520	90	1,000
Rendzina clay .	2,460	−131	−448	359	1,161	358	5,500
Chernozem clay .	2,350	−30	−105	115	185	−60	5,150
Bentonite . .	880	−130	−864	65	305	n.d.	5,400
Red soil clay .	1,750	−812	−968	15	0	n.d.	4,000
Black soil clay .	2,050	−122	−235	135	70	−25	10,550

It will be seen that sorption of iron, manganese, and potassium has taken place in the case of all the clays. The amounts sorbed by the chernozem, rendzina, and black soil are greatest and it is interesting to find that all these clays formed the darker complexes. Sorption of magnesium and sodium was, however, somewhat erratic. The available evidence is not sufficient to associate sorption of any one of the several inorganic constituents with dark colour production. But the cases of manganese and to a small extent those of iron follow somewhat closely the corresponding sorption of organic matter and black colour formation. Further support for these will be found in the results of similar experiments (Tables 7 and 8) with a homoionic clay (calcium) of the black soil with different volumes of a G-extract. It will be seen that under the more uniform conditions of those tests the amount of manganese is closely proportional to the organic carbon sorbed, increasing amounts being absorbed from the increasing volumes of the extract.

Base exchange capacity of the clays and their interaction products

The exchange capacity of the clays and their reaction products are given in Table 6. The black soil clay which has the highest exchange capacity gave the darkest colour. Bentonite with a higher exchange

TABLE 6

Base Exchange Capacity, m.e./100 g. Dry Clay

Sample	*Unperoxidized clay*	*Peroxidized clay*	*Peroxidized clay treated with G-extract*
Bentonite	64	. .	66·2
Black soil clay . . .	111	105·4	110·7
Red soil clay . . .	40	39	40

capacity than the red soil clay was the darker of the two. In the case of the red soil clay, other factors might have dominated so as to further

reduce the effect of its already low exchange capacity. On reaction with the G-extract, it remained unchanged. It is suggested by this that high exchange capacity of a clay is an important factor in the formation of a dark clay-organic complex.

The different behaviour of the black and red soil clays is worth noticing. The exchange capacity of the latter was almost unaffected either by peroxidation or by reaction with the G-extract. The black soil clay, however, was appreciably affected by both peroxidation and reaction with G-extract in respect of its base exchange capacity, the same value being obtained after interaction as before peroxidation. Assuming that the G-extract complexes have the same exchange capacity as the soil humus, the exchange-capacity of the interacted products should be much more than the value of 110·7 obtained since it contains about 3·5 per cent. carbon. The absorption has thus not appreciably contributed to the exchange capacity of the complex and may have resulted in reducing the total capacity. Similar effects of mixing organic and inorganic colloids of soils have been reported by Meyers (1937).

Nature of the interaction

Some attempts were made to find out whether the colour-producing reaction resembles an adsorption. It was found difficult to obtain fermented extracts under strictly reproducible conditions with different C:N ratios. The clay-G-extract reaction was, therefore, carried out with the same clay but with different volumes of the G-extract, i.e. with varying amounts of the reacting complexes.

One-gramme portions of the Ca-clay were treated with 20, 40, 60, and 90 ml. portions of the G-extract. The resulting clay-organic complexes ranged from light to very dark grey in colour, the intensity of the colour increasing with the amount of extract used. The amounts of carbon and nitrogen sorbed (Table 7) were roughly proportional to the quantities of the extract. The residual extracts were brownish-yellow

TABLE 7

C *and* N *sorbed by* 1 *g. of the Black Soil Clay* (Ca) *from Different Volumes of the* G-*extract*

Ml. of extract	*mg. sorbed*		
	C	N	C:N
20	6·85	1·45	4·72
40	13·60	2·83	4·80
60	22·85	4·23	5·40
90	33·80	7·03	4·81

and contained amounts of organic matter many times in excess of the amounts sorbed by the clay. This suggests that only a definite part of the organic matter of the extract was reactive and associated with the dark-colour formation. In Table 8 the amounts of some inorganic constituents sorbed from varying volumes of the extract are given. Iron

was invariably sorbed, but the amounts taken up were not proportional to the volumes of extract used. With increasing quantities of the extract, the iron sorbed increased to a greater extent. It does not appear to be due to replacement of aluminium from the clay mineral, as there is no corresponding increase in the amount of aluminium released.

TABLE 8

Cations sorbed in μg./g. of the Black Soil Clay (Ca-*saturated*) *from Different Volumes of the* G-*extract*

Ml. of extract	Fe	Al	Si	Mn	Mg	Ca	K
25 . . .	325	−330	−1,140	48	−180	−8,320	3,500
50 . . .	930	−347	−320	110	240	−9,890	5,850
100 . . .	2,300	−206	−303	190	100	−11,620	11,000

A greater amount of silicon came into solution when the quantity of the extract was small (25 ml.), but with larger volumes it appears that its solution was partially checked, probably because of the protection provided by the sorbed organic matter. However, because of the solubility of silicon (1,400 μg. per gramme of the peroxidized clay), it is difficult to get a clear idea of the activity of this element.

As pointed out earlier, sorption of manganese, though low in quantity, took place in all the cases and increased proportionately with volume. Sorption of potassium was again appreciable in all cases and the amount sorbed was, to some extent, proportional to the volume of extract. Sorption of magnesium was variable in extent. The release of calcium from the clay is not unexpected, the clay being calcium saturated and containing approximately 1 m.e. Ca per gramme. However, it may be noted that the amounts displaced did not increase proportionately with the increasing volumes of the extract, and only about half the exchangeable calcium was released by 100 ml. of the extract. Thus, it appears that an appreciable amount of this element became closely associated with the clay-organic complex.

Influence of exchange cations on the sorption

Homoionic preparations of a peroxidized black soil clay containing Ca, Mg, Na, and H were prepared by repeated treatment with the chlorides of the elements and treated with 100 ml. portions of G-extract. The resulting products were analysed for carbon and nitrogen content and the extracts analysed for the mineral constituents. The results are given in Tables 9 and 11.

The Na-clay retained a marked gel-like form and appeared three times as voluminous as the other clays. All the products were dark grey, the darkness increasing in the order H < Ca < Mg < Na. The amount of organic matter sorbed was also in the same order. The C:N ratio of the sorbed matter has the same value in all cases and is about 5 to 6 as in previous experiments. It appears probable that the nature of the complexes sorbed is not affected by the exchange cations although the amounts sorbed and depth of colour produced are markedly influenced

by them. It may be pointed out that in these reactions, the exchangeable bases of the clays were not the only cations involved. The extract itself

TABLE 9

Carbon and Nitrogen sorbed by the Clay

Sample	*pH of the extract*	*mg.*		C:N
		C	N	
Ca-clay of black soil . .	5·02	36·47	6·61	5·52
Mg „ „ „ „ . .	5·0	52·65	8·98	5·86
Na „ „ „ „ . .	4·95	58·77	8·89	6·61
H „ „ „ „ . .	4·45	27·98	6·69	4·18
Ca „ „ „ „ $+CaCO_3$.	5·85	35·68	6·99	5·1

contained amounts of K, Ca, Fe, Mg, Mn, totalling some 2·2 m.e. per 100 ml., or twice the exchange capacity of the amount of clay used. Thus the system was a heterogeneous one with regard to the

TABLE 10

Cations in G-extract in mg./100 ml.

Fe	Al	Si	Mn	Mg	Ca	Na	K
5·0	0·28	3·63	0·93	4·08	10·4	2·59	52·0

effect of any individual cation, but in spite of this appreciable differences were indicated in the amount of the organic matter sorbed by the same clay with different cations.

TABLE 11

Cations sorbed in μg./g. clay from 100 ml. G-extract

Sample	Fe	Al	Si	Mn	Mg	Ca	K
Ca-clay of black soil .	2,100	−275	−315	135	240	n.d.	10,600
Mg. „ „ „ „ .	2,150	−545	−430	260	−5,715	2,250	12,700
Na. „ „ „ „ .	2,230	−450	−235	340	1,095	1,600	16,400
H „ „ „ „ .	2,480	−253	−490	355	305	2,790	13,300
Ca „ „ „ „ . $+CaCO_3$	2,970	−102	−580	190	−365	n.d.	10,600

The sorption of inorganic constituents (Table 11) is again similar in all cases and resembles the sorption with the clays of different soils.

Influence of pH on the sorption

The pH of the freshly prepared G-extract was 4·64. This pH is very low in relation to the black soils which generally have a high lime status and a pH of over 7·0. It was, therefore, attempted to study the reaction over a range of pH. The values of pH arbitrarily chosen were 3, 5, 7, and 9, the pH of the reaction mixture being adjusted with very dilute

hydrochloric acid or with freshly prepared calcium hydroxide. Blank determinations were carried out on G-extracts alone at all four pH values. The pH values of the samples were checked and adjusted every alternate day. In Table 12 the amounts of carbon and nitrogen of the sorbed organic matter and of the corresponding blanks are given. It will be seen that maximum sorption took place at pH 5, a little less at 3, much

TABLE 12

Carbon and Nitrogen sorbed by the Clay at Different pH Values

Sample	*pH*	*mg. present*		*mg. sorbed*		C:N *of the sorbed org. matter*
		C	N	C	N	
Clay-G complex . . .	3	29·58	5·85	22·23	4·64	4·8
G extract alone . . .	,,	7·35	1·21			
Clay-G complex . . .	5	41·49	7·97	24·49	4·68	5·2
G extract alone . . .	,,	17·0	3·29			
Clay-G complex . . .	7	40·98	7·51	10·48	2·48	4·2
G extract alone . . .	,,	30·5	5·02			
Clay-G complex . . .	9	31·2	4·47	0	0	..
G extract alone . . .	,,	31·7	4·51			

less at 7, and none at 9. The intensities of the dark colour produced were in the same order. The product at pH 9 was unchanged in colour and there was a thin dark layer of unreacted organic matter on the surface of the clay. A similar but thinner layer was formed on the product at pH 7; those at pH 5 and 3 were uniformly dark coloured with no visible distinct deposit of organic matter. It may be pointed out that the carbon content of the deposit in the centrifuged blank was nearly equivalent to the carbon content of the reaction product at the same pH. It is therefore possible that the colour-producing reaction could not take place at the high pH as the reactive organic complexes of the G-extract might have been rendered insoluble and non-reactive by the higher concentrations of calcium ions added as $Ca(OH)_2$ to raise the pH.

In Table 13 the figures for some inorganic constituents present in

TABLE 13

Cations present in G-extract (mg./100 ml.) at different pH values after Atmospheric Oxidation

pH	Fe	Al	Si	Mn	Mg	K
3	6·0	0·525	1·75	0·905	3·465	51·0
5	3·575	0·35	2·75	0·92	3·465	50·6
7	1·675	0·126	2·75	0·48	3·285	50·05
9	0·875	0·075	2·75	0·013	3·04	52·05

extracts alone after atmospheric oxidation are given. The amount of silicon at pH 5, 7, and 9 is the same, while, as would be expected, a portion was precipitated at pH 3. Considerable differences existed in the concentrations of iron, and also to some extent of manganese, aluminium,

and magnesium. The lower values obtained with increasing pH indicate that aluminium and manganese were probably separated as hydroxides and carbonates or as complexes with the organic matter. It was seen earlier (Table 12) that the amount of organic matter separated from the extracts increased with the increasing pH. Ordinarily, greater amounts of organic matter should go into solution at pH values above 7, but as

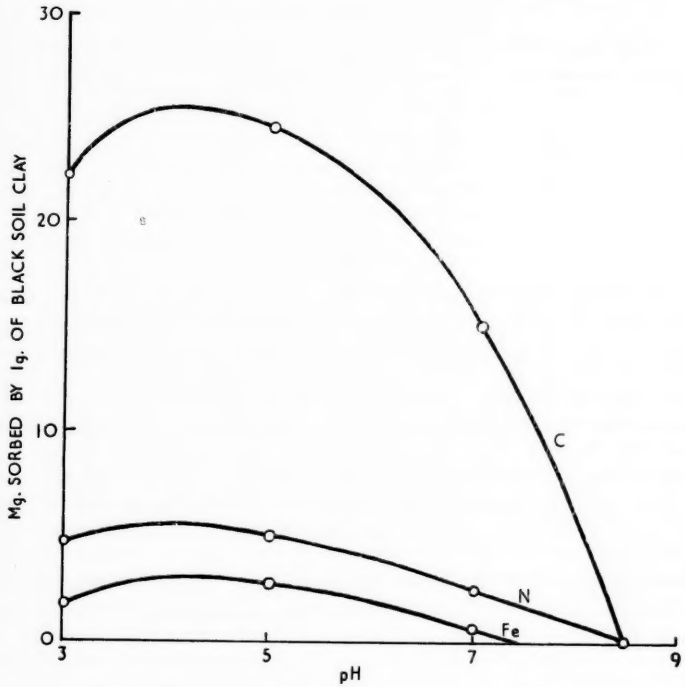

FIG. 1

this was not so in this case, it seems that the inorganic constituents were probably in complexed forms with the organic matter and presumably these complexes were inactive at the higher pH reactions.

The amounts of the inorganic constituents sorbed by the clay at different pH values are given in Table 14. The amounts of sorbed iron followed somewhat the same trend as the sorbed organic matter, particularly the nitrogenous fraction. This is more clearly shown in the accompanying graph. The above trend was not so closely followed by manganese. Sorption of potassium was very variable and in all cases was independent of the pH. Magnesium was released from the clay at acid reactions, the quantity decreasing with an increase in pH; at pH 9 a small amount was sorbed from the extract. Magnesium in this case might not have been associated with the organic matter. It appears that

a higher pH favours fixation of magnesium on the clay. The negative sorption of aluminium both in acidic and alkaline media does not appear to be explicable only on the basis of its solubility from the clay. It is probable that it was displaced by iron in the acidic medium and by magnesium in the alkaline medium. Negative sorption of silicon was somewhat expected in view of its solubility at acid or alkaline reactions.

TABLE 14

Cations sorbed by the Clay (μg./g.) at Different pH Values

pH	Fe	Al	Si	Mn	Mg	K
3	1,725	−275	−292	25	−550	7,450
5	2,575	−124	0	165	−365	10,550
7	575	0	−23	206	−60	8,250
9	0	−53	−1,355	0	245	11,900

Discussion

Singh (1954*b*) has shown that the colour of black soils is due to a contribution of their organic matter and perhaps arises from its specific composition as red soils of the same geographical region contain as much organic matter as the black soils. From considerations of its actual genesis, the soil organic matter should be a product of aerobic as well as anaerobic decomposition of raw organic matter, such as pasture grasses, by the soil organisms. A study of the colour produced and of the associated reactions with the two reacting systems of decolorized soil clay and fermented grass materials should have several aspects which are related to the production of dark-coloured complexes in natural soils.

Interaction of various clays with extracts of anaerobically fermented grass showed that illite, bentonite, and the clays of the chernozem, rendzina, and black soil—all of which are rich in montmorillonoids—became very dark. Kaolinite and red soil clay, in which kaolinite is the dominant clay mineral, in contrast, did not change appreciably in colour. However, the amount or the C:N ratio of the organic matter sorbed by the red soil clay was not remarkably different from that sorbed by other clays under similar conditions. Thus, it appears that even if the added organic matter is somewhat similar, only certain types of clays can form a dark clay-organic complex. One of the main conditions for this to take place seems to be that the clay should have a high exchange capacity, presumably causing a high dispersion of the organic matter on its surface. The presence of iron oxide in finely divided condition in the clay or of iron compounds in the grass extracts (above, p. 47) results in a suppression of colour production, but not with the sorption. Probably an entirely different set of organic complexes is engaged, and this may afford an explanation of the differences between related occurrences of black and red soils in respect of their organic matter content and coloration.

The role of exchangeable bases in the clay/extract reaction was quite

remarkable with regard to the amount of organic matter sorbed and to the intensity of dark colour developed. Sodium clay sorbed the greatest amount and gave the darkest product, which may be partly due to the greater degree of dispersion. Another reason may be a very low energy of replacement of sodium as compared with the other cations, thus enabling a greater amount of the organic matter to form complex with the clay minerals. Regarding the natural occurrences, it may be suggested that if they contain even a small fraction of exchangeable sodium, they would certainly appear darker. Working on the tirs of Morocco, del Villar (1944) pointed out that the dark coloration of these soils is more intense if there is sodium present to disperse the soil. There are similar low-lying occurrences of dark-coloured soils in other parts of the world, particularly in the tropics and sub-tropics, which retain in their solum appreciable amounts of sodium. It is very likely that this element increases the effectiveness of their basic dark colorations.

There is not much evidence available for an exchange character in the reactions of the inorganic constituents. Invariably, the reaction results in sorption of all ordinary exchangeable basic constituents of the acidoid clay such as Mg, Ca, K, Mn, or Fe. The amounts sorbed are, however, of considerable magnitude. The only other possible way in which these constituents could be sorbed is by interaction with the constituents of the clay lattice by fixation. Some such reaction is strongly indicated by the uniformly negative character of the absorption of the two lattice components Si and Al. It appears that black soil clay interacts with organic complexes of the grass extract with loss of silicon and aluminium from its lattice. Such loss should give rise to alumino-silicates of different SiO_2:Al_2O_3 ratios from that of the original clays with consequent change of its exchange capacity. Determination of the exchange capacity of the clay-organic complex has shown that this property is not necessarily additive and that the complex has probably a lower exchange capacity than that of the clay and organic components separately.

The fermented grass extracts, in most cases, were characterized by a C:N ratio of 5, and in all cases the ratio in the coloured complexes remained the same. This feature is independent of the source of the clay, its exchange composition or the pH of the reaction, the absorption taking place in such a way that complexes with the same C:N ratio are sorbed. It has already been pointed out that the sorption proceeds towards the attainment of a saturation limit rather than an equilibrium one. Increasing quantities of extract of the same concentration lead to proportionately increased sorption of complexes with the same C:N ratio. The reaction is not perhaps one of simple adsorption as the residual extracts contain organic matter many times in excess of the amounts sorbed by the clay. It is probable that only the reactive nitrogenous constituents of the extract are irreversibly or chemically sorbed to give stable clay-organic complexes.

Of considerable interest are the results of the studies of a sorption of inorganic constituents. These, it may be pointed out, were determined by difference of the amounts present in 100 ml. of the fermented extract

before and after reaction with the peroxidized clay. Some such characteristics of their sorption as the uniformly negative character of the sorption of the components of the clay-lattice have been pointed out already. All the constituents studied were sorbed differently by different clays, potassium to the greatest extent. The amounts of manganese sorbed perhaps deserve special notice. Generally, the amount of this element sorbed follows more or less closely the amount of carbon sorbed and with identical reacting solutions the amounts taken up are proportionate (Tables 7 and 8).

The effect of pH on the reactions indirectly suggests that anaerobic conditions are necessary for the formation of the homogeneous and dark clay-organic complex as present in black cotton soils. Sorption was at a maximum near pH 5, much lower at pH 7, and was not apparent at pH 9. The darkness of the products was in the same order, at pH 9 the colour being unchanged. Meyers (1937) found that the tendency of organic colloids to combine with inorganic soil colloids was most marked under acid conditions. Ensminger and Gieseking (1939) also showed that albumen and gelatin were more completely adsorbed in suspensions with high hydrogen-ion concentrations than in suspensions with low hydrogen-ion concentrations. The results of the present study are in general conformity with the findings of the above workers. It will be recalled that the black cotton soils invariably give overall pH values higher than 7, the alkalinity being mainly due to their base saturation and $CaCO_3$ content. The presence of $CaCO_3$ in the reacting phase should neutralize the acid character of the humic matter and this may be expected to result in an appreciable reduction of sorption and colour production. This view is supported by the observation made in the course of these studies, that addition of $Ca(OH)_2$ to the fermented extracts results in a precipitation of some fractions of the organic matter of the extracts. This is not a consequence of the resulting change in pH of the extract, but rather is due to the formation of insoluble compounds, probably the colour-forming ones.

In view of these observations, the existence of local acid conditions in these soils, at least for some weeks in the year, appears to be necessary for the formation of the homogeneous and dark clay-organic complex. It was mentioned earlier that the pH of the anaerobic systems is usually somewhere near 5. In the black cotton soils, because of their low-lying situations or impeded drainage, anaerobic conditions would probably prevail during the wet seasons and these consequently would almost certainly produce localized slight acidities in the solum. These would tend to be obliterated later by swelling and shrinking effects which would also lead to the thorough mixing up of soil and subsoil.

Summary

A study of the reaction of different clays with anaerobically fermented grass extracts has been carried out with a view to determining the effect of various factors on the formation of a dark-coloured clay-organic complex. Montmorillonoids and other high base exchange clays have been

shown to favour the formation of the dark clay-organic complex, the organic matter being in a highly intimate state when associated with them.

A study of the effect of exchangeable bases on the reactions showed that sodium clays sorbed comparatively higher amounts of organic matter and gave distinctly darker products than the H-, Ca-, or Mg-clays.

It has been shown that sorption of the organic complexes and consequent formation of the dark clay-organic complex did not take place at pH 9, and was less apparent even at pH 7, but at lower reactions (pH 5 and 3) appreciable amounts were sorbed, and the products formed were very dark in colour, resembling the original clay. The observation suggests that the formation of black cotton soils only takes place under at least periodic anaerobic conditions, as only then can these soils, with the overall pH of 8, develop slight acidities.

The nature of the sorbed organic matter, as indicated by its C:N ratio, does not appear to differ from clay to clay, with changes in the exchangeable bases or with variation in pH, suggesting that only a certain part of the extract was active in all the cases.

The sorption of organic matter, and the formation of a dark coloration, was invariably associated with the sorption of such inorganic constituents as iron, manganese, calcium, and magnesium. It is probable that these inorganic constituents also contribute to the dark colour formation of the clay-organic complex.

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THE CLASSIFICATION OF SOILS

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WHEN scientists discuss methods of analysing a solution for traces of phosphate, they are practical, reasonable, and unemotional. When the same men discuss the classification of soils, these virtues are liable to evaporate. Partly this is because national prestige is felt to be at stake; but still more, because so few workers are clear about what they are doing and why they are doing it.

Some of the fog that envelops our subject comes from the confusion of soil with land or landscape. This article deals with the classification of soil profiles and not of types of land. In spite of this restriction to the smaller and simpler problem, the principles here set out must apply equally to the larger problem, though a different coding system would be called for. In fact, the principles are so simple that they must have occurred to many people in many fields at different times; the excuse for setting out these platitudes here is that they do not seem to have occurred to many workers in soils.

One obvious reason for classifying is to save time and simplify our descriptions. If many of the soils that we meet have three or four properties in common (say, a uniform texture down the profile, strongly aggregated clay, and a red colour) it is sensible to use one short name for them all. This practical approach has been used both in the United States of America and in Australia. If we accept it, we have to solve a problem of technique and arrangement. In brief, we may agree that fifteen to twenty properties of a profile are worth considering. Most of these can be written down as yes-or-no. Thus a profile may or may not have uniform texture, may or may not be acidic throughout, may or may not have a peaty horizon. Each of these properties may be put symbolically as A or a, B or b, &c., so that the problem consists of sorting out a large number of individuals like A B c D e F G h ..., a B c d e F g h ..., and so on. This problem is discussed in some detail below.

But before we can deal with this problem, we must deal with the people who dislike the way in which I have put it. These people belong to two overlapping groups. First there are those who believe that the classification of soils has already been pretty well done by a few great men, that we already know the answers more or less, and that all that has to be added is a little tidying and a supplementary edition to include more tropical soils and other oddments. Those of the second group feel that the subject of pedology is too dignified for the down-to-earth treatment of the preceding paragraph, and that a real classification must use genetic hypotheses.

The people who imagine that the job is already done can be disposed of first. They will simply be asked to point to the various combinations among those listed that fit their names of chernozem, braunerde, and

the rest. When they have done this, either they will see for themselves how confused their concepts are, or (if I am wrong) they will be able for the first time to explain to the rest of us what their criteria really are. The main stimulus to efforts at clarification, such as the present, is the despair which besets any critical reader of the literature on account of the wide spread in the usage of most of the technical terms.

Those who believe that a classification must be genetic in order to be respectable might be reminded that plenty of classifications exist which are respected and are not genetic; for example, those of chemical compounds and viruses. Since soils have not common ancestors, while plants and animals have, the case for attempting a genetic classification of soils is poor from the start. In any case, dignity has no place in science. Classification is a practical job, like any other piece of analytical work.

We may now return to our main problem, and the matter-of-fact approach. First, can we draw up a bifurcatory scheme at all? This implies that the choice of A or a is so important that it outweighs all others; B or b outweighs all those below, and so on. Thus we have an unambiguous scheme of classification. We may stop at any stage that we please. If we decide on having sixty-four major divisions, we pick the six most important properties ($2^6 = 64$). This scheme can be improved somewhat without surrendering any principle. It may be that, among the A's, we are interested in whether the soil is B or b, but not in whether it is C or c, while among the a's the reverse holds—we are only interested in the choice C or c.

In this way we might achieve a list along the following lines (abbreviated here in order to show the principles):

ABCD	aCD
ABCdE	aCdE
ABCde	aCde
ABcD	acDFG
ABcd	acDFg
AbDF	acDf
AbDf	acdG
Abd	acdg

This list is achieved by simple bifurcation, and all the 128 possible combinations of ABCDEFG with abcdefg must find a place in it. It is self-consistent, and cannot fail.

We may compare this with an extreme case in which a new criterion is used at every stage for every class, as below:

ABDH	aCFN
ABDh	aCFn
ABdK	aCfO
ABdk	aCfo
AbEL	acGP
AbEl	acGp
AbeM	acgQ
Abem	acgq

Such a subdivision might occur in some sections of the Linnean scheme for plants. The total number of possible combinations of these fifteen characters (A to Q) is 2^{15} or 32,768, of which only sixteen are chosen. But in the Linnean scheme, the vast majority of these rejected combinations do not exist, and we may not be interested in others that do exist. Here lies a difference between soils and plants; there are fewer usable criteria for soils, and these must crop up at various points in the scheme, so that our first group of sixteen represents our kind of problem, rather than the second sixteen.

While our proposed subdivision (ABCD, ABCdE, &c.) is consistent and cannot fail, it may not give satisfaction. We have started by supposing that people agree that the properties listed are of the order of importance here given—that is, that A is most important, B next, and so on. This agreement has been achieved with plants, but we may not achieve it with soils. In fact, this is one reason for our present confusion. Thus, in the above list, we put ABCdE in the same major division as AbDF, because we think that A matters most. But what can we say to a critic who wants instead to group ABCdE with aCdE because they have CdE in common?

It seems to me that there are three answers, the first of which is useless while the second and third are sensible.

1. We may agree with him and resolve to have no order of priority, but to put together those soils which have nearly all their properties in common—say, any four out of a list of five, or any eight of a list of ten. This principle has been widely used in a loose and unconscious way, but it can be shown to be merely a source of confusion. Thus, if we agree to put together all soils that have at least four of the five properties ABCDE, then how many others of the possible combinations can we count? We cannot pick a group like ABCde because, if we did, we could not tell where to place a soil like ABCDe, which might equally well belong to ABCDE and ABCde. If we make an arbitrary decision that it belongs to the former, we are breaking our rule that there is no order of priority. So we come down to ABcde and abcDE—and there we must stick. We cannot include abcde, for example, because then we could not say where abcdE was to go (see the two last groups). Thus, out of all the thirty-two possible combinations of these five properties, we are left with three at most, and these are not sensibly chosen. Clearly, this attempt is useless.

2. We may tell him that we sympathize with him, but that we have to keep to the rules. While the rules are arbitrary they are made so as to be as tolerable as possible to as many people as possible. There is no way of proving that we are 'right' in picking the question 'A or a?' as our first question. There is no such thing as right or wrong in a classification. We classify for our convenience, and if our colleagues will use our scheme and it is consistent within itself, we should not ask for more.

3. But he may persist in his objections. Who are we to say that ABCdE goes with AbDF and not with aCdE? We must now admit

that we are only well-meaning people, that we try to give satisfaction and that we can do no more. If enough people object, we must give in. Two courses can follow.

(*a*) We may simplify our list of order of importance. We may make AaBbCcDd all of equal order, and EeFfGgHh also of equal order, but below ABCD. We now have pigeon-holes for each of the sixteen combinations of the first four (A or a, B or b, &c.); in fact, the number may be less than sixteen, since some combinations may not exist. The second group similarly gives sixteen (or fewer) subdivisions for each of the original sixteen; again the total number at the end of this step is below the maximum of 256 because not all combinations exist, and the total may be of the order of 100. In this way we have simply a catalogue of major kinds of soil, which may be known by names or by code numbers. We can put these generalized soils on to maps if we wish to do so. On the other hand, we no longer pretend to show any analogy to the exact dichotomous schemes that some people admire.

This was the procedure used by an Australian committee (B. E. Butler, R. G. Downes, G. W. Leeper, C. G. Stephens, L. J. H. Teakle) and presented to the International Society of Soil Science in 1954. It will be noted that it does not completely answer the objection about the order of importance of characters, since it implies that Dd is more important that Ee; but it greatly reduces the area of possible disagreement.

(*b*) But we may decide that if nothing better than this catalogue can be made, a complete and exclusive scheme is not worth having. This means that no scheme exists that can be put on a map, since a map demands mutually exclusive classes. It may come as a shock to some pedologists to realize that classification need have nothing to do with mapping; but once this step is taken, we are already on our way out of the fog. Even if we abandon a complete scheme, we can still, however, use some of our short and convenient expressions. We may find that combinations like AbDF, CdE, DGHm, and so on occur so often that we want words for them. We already do this when we talk of claypan soils or soils with bright red tints or soils with bleached horizons. Any of these may overlap, and perhaps we should not mind.

The organic chemist has a similar problem. He has alcohols, aldehydes, carbocyclic and heterocyclic skeletons, amines, ortho and meta and para relations, carboxylic acids, and dozens more groups. He has compounds that combine five or six characters at once. But he does not worry, and does not search for a grand system of classification to raise his self-esteem. He will think of his compound for one purpose as a carboxylic acid, for another as an aldehyde, and for another simply as a meta-compound.

W. L. Kubiena can be regarded as the spokesman for the opposition to a matter-of-fact, analytical approach, especially because his book *The Soils of Europe* will be used as a standard for reference for many years to come. In spite of the merits of the book, I think that his views on classification are illusory.

Kubiena claims to follow a 'natural' system which orders his objects according to *all* their characteristics and not on the basis of only a few properties, a basis which according to him would be 'artificial'. In this arrangement he claims that there is no arbitrary principle of division, but 'the essential order of Nature itself is represented'.

Two comments can be made immediately. Firstly, this is the very thing that Kubiena does *not* do; secondly, the notion is impossible. Kubiena's classification gives particular weight to his own speciality, namely, the appearance of the soil under the microscope, especially the state of ferric colloids. As an indication of how he follows his own enthusiasms, we may note that he places differentiation of texture (inorganic colloid) so low in the scale that it does not appear as a profile character in his hundred or so varieties of terrestrial soils. This is literally an arbitrary decision (*arbiter* = judge). Many people, including myself, disagree with his decision and think that it might be reversed in a court of appeal.

We are concerned here with principles and not with details, so we need not consider further whether the pattern of flocculation of ferric sols is more important than, say, a bleached horizon. All that needs to be done here is to destroy the illusion that there is some 'essential order in Nature itself' that we have to discover. If there is, who is to decide which discovery is right? Has Kubiena received a revelation? If four different revelations come, say, to an Austrian, a Russian, an American, and an Australian, are their countries to vote on it?

But of course this is all absurd and there is no answer.

Nobody can blame Kubiena for not taking 'all their characteristics' into account, because it is impossible. We do not even know *all* the characteristics. Among those that we do know, we must start somewhere, so we ignore some that we regard as trivial. This is how all classifications are made. We might ask the devastating question, How many characteristics must be brought in so as to convert an 'artificial' scheme into a 'natural' one? Six? Ten? Fifteen? Whatever the answer is, those who use the matter-of-fact analysis will be ready.

We might pursue here the often repeated doctrine, allied to Kubiena's: namely, that a classification that uses many properties must be superior to one that uses only one or a few properties. This doctrine is strange on the face of it. Either the many properties are always found together or they are not. If they are, any one of them will suffice as a criterion. If they are not, the more there are of them the more complex the classification must be; so we have gained nothing and we are forced to decide, as above, on an order of importance if we are to end with a manageable number of groups. How could anyone have taken such a doctrine seriously? It appears that it originated in a misunderstanding of an argument current during the nineteenth century, namely, that if one criterion carries with it three or four properties which are always associated, it should be used in preference to a criterion which has no associations. This argument is sensible enough; but it loses all sense when it is expanded into the form seen at the head of this paragraph.

Or perhaps more likely, the doctrine has been mistakenly carried over

from zoology. Where there are *very many* criteria possible, one may ask for a group to have any four properties out of a given five, as in our earlier example of including ABCDe with ABCDE. So long as the nearest group in the scheme is abcde, which might include say abCde but no more capitals than one, this will work. But five criteria have been used up, and in the field of soils we have too few available criteria to be so spendthrift.

Finally, let us dispose of the word 'artificial'. This should mean 'the work of man', and since man makes his own classifications, all our classifications are artificial. We may condemn a classification because it is trivial or useless or cumbersome or irrelevant or inconsistent, but not because it is artificial. Unfortunately, the English word carries an aura of disapproval. Scientists should do all they can to dispel this aura. The word should be descriptive and unemotional. There are natural lakes, and there are artificial lakes. But all classifications are artificial, and none of them is any the worse on that account.

An attempt at clarification, such as this, must be the result of discussion and collaboration even more than most contributions to the progress of science. While one cannot disentangle all the parts that one's fellows have played, I must acknowledge, in particular, the help of the four colleagues mentioned on page 62, without necessarily involving them in all the above arguments.

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COLOURED PHOTOGRAPHS OF SOIL PROFILES

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WITH TWO PLATES

MONOCHROME photographs have been found satisfactory for recording the shape of structural units and some other morphological characters of soils. It is, however, generally necessary to have a record of the actual colours of soil profiles and these are frequently badly reproduced owing to the use of unsuitable materials and techniques.

It is the intention of this paper to outline a technique involving the use of two cameras and Munsell Soil Colour Charts (1949) which has resulted in the production of colour photographs of soil profiles up to natural size with a satisfactory reproduction of the original colours.

After a suitable profile pit has been dug so that the face to be photographed faces the sun (it is important to have direct sunlight) two photographs are taken, one on monochrome film and the other on colour film for the production of transparencies. It is not necessary to use a scale indicator with the monochrome photograph but it is important to use one for the colour photograph. A sketch diagram is made of the profile with measurements. The various colours appearing in the profile are recorded by means of Munsell Soil Colour Charts. If required hand specimens can be collected.

The films are then processed. The colour photograph is mounted in the form of a lantern slide, while from the monochrome negative an enlargement is made.

In taking the photographs the choice of camera is the first consideration. In order to get good enlargements it is necessary to have a good negative. Obviously the larger the original negative the better will be the final enlargement but as negative size increases, so also do the size and weight of the camera, therefore a compromise must be sought. This has resulted in the choice of a 120 or 620 camera. It is essential that the camera should have a really good lens and be capable of focusing down to short distances. A 35-mm. camera is used for the colour photographs, because many of the colour films at present manufactured are made only in that size; they are relatively economical; and the transparencies can be used for lecture purposes as 2×2 in. lantern slides.

For both the monochrome and the colour photographs reflex cameras have been found to be ideal.

The choice of film is the second consideration. As the monochrome photograph is to be enlarged it is necessary to use a film of very fine grain and to follow this up by careful processing, using a so-called fine grain developer.

The choice of colour film is somewhat more difficult as nearly all the films commercially obtainable at present fail to reproduce accurately one or more colours. This failure can sometimes be rectified by the use

of an appropriate filter. In order to reduce the number of filters a film of the widest possible latitude should be chosen.

The techniques involved in processing films and in making enlargements and lantern slides can be found in many standard textbooks on photography (e.g. 1954, pp. 451–9). It should be mentioned, however, that the photographic paper used should be pure white with a dead matt surface.

The size of the enlargement depends upon personal choice. An arbitrary size can be chosen or they can be made on a standard size of photographic paper. It has been found that 15 × 12 in. photographic paper is very suitable for the enlargements, giving finished photographs up to 14 × 10 in.

Since the correct colours can be more easily reproduced on a brown base than on a black and white one, the monochrome enlargement is sepia toned, preferably by the Sulphide Toning method (l.c., p. 315).

After drying, the enlargement is hand coloured using a good brand of transparent photo oil colours. The application and working up of the colours is guided by the colours present in the transparency, the Munsell Soil Colour Charts, and any hand specimens that may have been collected at the time the photographs were taken. The colours are now allowed to dry and then the photograph is mounted on cardboard, suitably annotated and framed behind glass.

This method has been found to be a very useful and satisfactory way of making soil colour photographs (Plates I and II) because the final colours can be controlled and any inaccurate rendering of colours in the transparencies corrected by using the Munsell Soil Colour Charts and hand specimens. Such photographs can be used for illustrating lectures, for museum collections, and for standardization of visual descriptions of soils in different areas and by different observers. It has been found that such photographs are in many respects superior to soil monoliths because they maintain their freshness and are more representative of the original soil profile than a monolith which dries out and cracks in a very short time, even when using one of the more recently developed methods.

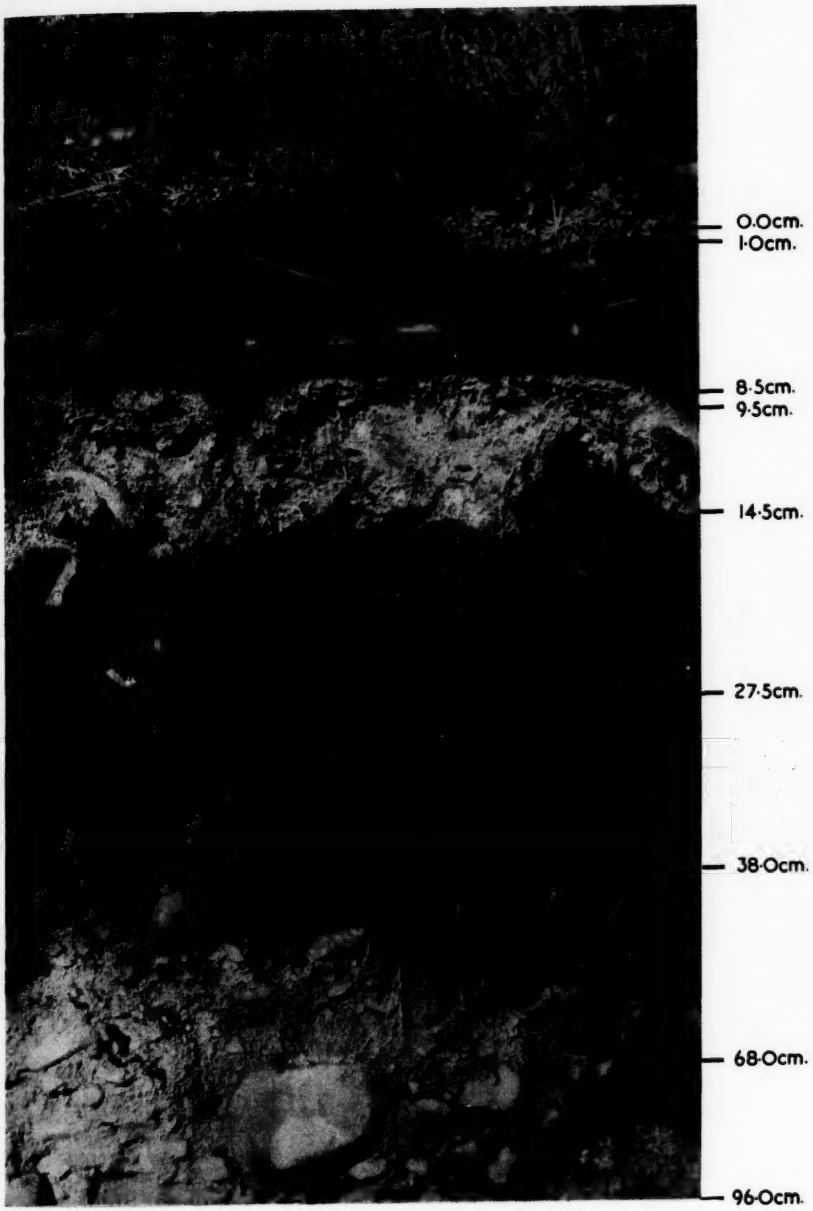
This method has been in constant use in this Department for the past two years and the original photographs which were taken are still very fresh in appearance while the monoliths taken at the same time are almost worthless.

Summary

A technique for the production of illustrations of soil profiles in their natural colours is described. This involves the use of two cameras and Munsell Soil Colour Charts.

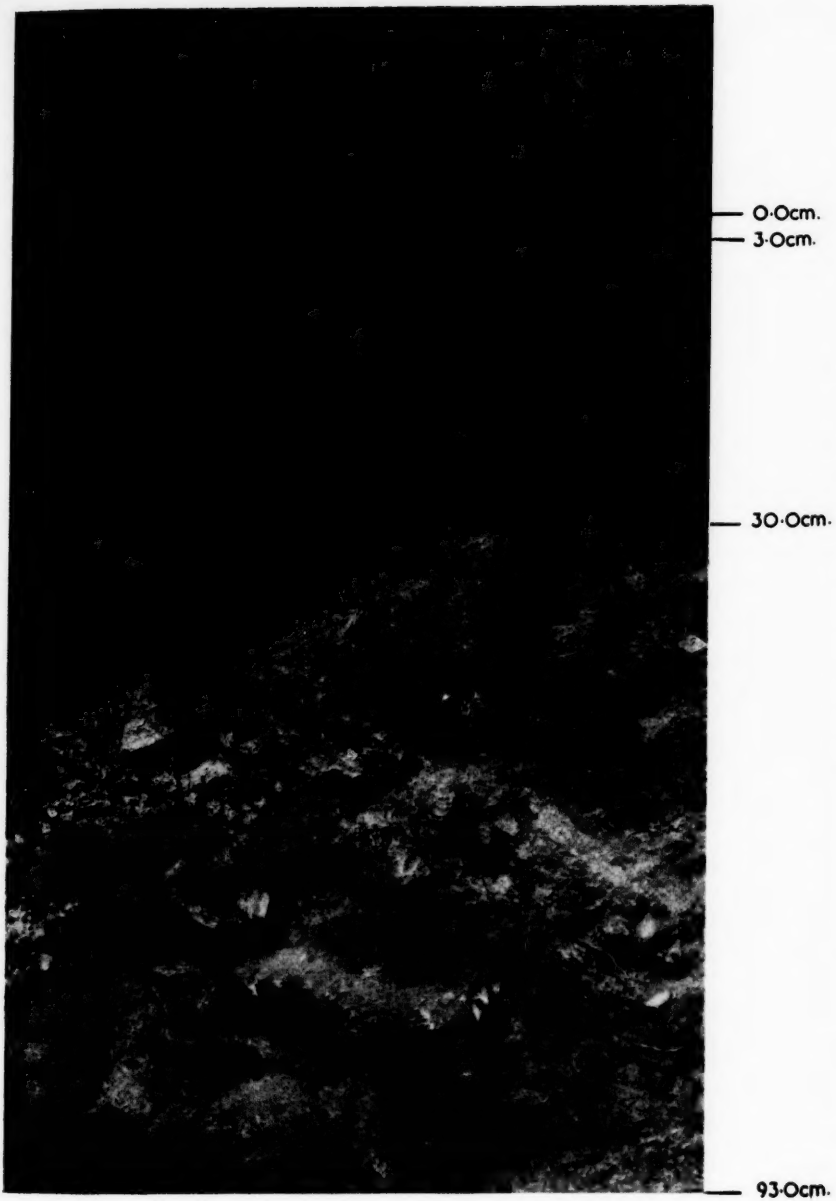
A colour transparency and a monochrome photograph are taken at the same time. The monochrome is enlarged to a suitable size and sepia toned. With the aid of the colour charts and the colour transparency the photograph is hand coloured to the correct shades of the natural profile.

I would like to express my indebtedness to my father, Mr. E. A.



Scots pine forest soil. Compartment 2: Dalliefour Wood, Alltcailleach Forest, Ballater, Scotland. 1953

E. A. FITZPATRICK—PLATE I



Heathland soil. Compartment 37: Alltcailleach Forest, Corrie Burn Basin, Ballater, Scotland. 1953

E. A. FITZPATRICK—PLATE II

FitzPatrick, Bridgetown, Barbados, B.W.I., who instructed me in the art of photography.

Grateful acknowledgement is also made to the Carnegie Trust and the University of Aberdeen for grants towards the cost of publication of the plates in this paper.

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A RAINFALL TEST FOR STRUCTURE OF TROPICAL SOILS

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WITH ONE PLATE

Summary

The ability of the soil surface to accept continuous heavy rainfall is a critical factor in the prevention of accelerated erosion of tropical soils. The qualities required in the soil are complex, and are not easily inferred from simple laboratory measurements. A direct test has therefore been developed for this property. Large soil cores of undisturbed structure are brought to a standard moisture tension, and are subjected to heavy artificial rainfall of controlled drop-size and intensity. The drainage tension is maintained at a constant value, and the rate of infiltration is measured. The apparatus is described in detail. Examples of results from a tropical rotation experiment are given, in comparison with pore-space and percolation measurements.

Limitations of Soil-Structure Measurements

RAINFALL acceptance is a complex effect. Firstly, there must be sufficient stability in the upper few millimetres of surface soil to avoid slumping and sealing under the mechanical violence of striking raindrops. Secondly, the permeability of the underlying soil must be adequate to transmit the water accepted by the beaten surface. Neither of these effects is simple, since they both involve the stability of dry soil to rapid wetting, and the stability of wet soil to dispersion by moving water. Measurements of any one of these effects in the laboratory, or their separate evaluation by different techniques, have not yet provided an adequate assessment of the field behaviour of soils in the range of structural conditions occurring in tropical agriculture. Surface effects are accentuated in the tropics by the alternation of severe desiccation and of high-intensity rainfall. In the course of studies in field and laboratory of structural changes in lateritic East African soils (Pereira, 1954) wet-sieving methods were found to give arbitrary results which varied with details of technique. Tension-table measurements on undisturbed soil cores gave results more closely in accord with field observations. For tropical soils there is a need for a routine method which gives full weight to the sealing effects of rainfall on the soil surface.

Testing of Soil by the Impact of Waterdrops

Ellison (1944, 1952) distinguished the separate effects of erosion by run-off and of soil-splash by raindrops, and devised a 'splash-catch' test for the comparison of erodibility of different soils. He estimated the dispersion of aggregates by wet-sieving of soil samples before and after exposure to artificial rain. McCalla (1942) counted the number of drops, of 4 mm. diameter, required to drive single soil aggregates through a 1-mm. screen, and expressed the results in terms of the kinetic energy of

the water. Smith and Cernuda (1951) developed McCalla's technique for application to tropical soils, and found preliminary wetting under reduced pressure to be necessary. Low (1954) has used a modification of McCalla's technique for English soils. Although these methods constitute an advance from wet-sieving techniques, they test only part of the mechanism of soil capping. The blocking of pore-space by the dispersed soil is an effect which involves both the degree of the dispersion and the distribution of the pore sizes, as shown clearly in the microphotographs by Duley (1939). It cannot therefore be tested adequately on single crumbs. It may well be affected by the difficulties of standardizing the packing when samples of disturbed soil are used, as in the methods of Duley and Kelly (1939), McCalla (1942), and of several workers in recent studies of synthetic soil conditioners, all of whom have spread layers of disturbed soils on sloping trays and have sprayed them with water. Bean and Wells (1953) explored the problems of soil capping by allowing drops of various controlled sizes to achieve terminal velocity before striking dishes of soil. They found capping to increase rapidly with drop-size and their results emphasize the need to use large drops and to standardize their sizes.

Direct application of artificial rainfall in the field is a desirable method of measurement, but the various field equipments developed in the U.S.A. and in Australia for this purpose would be difficult to operate under East African conditions of roads and water supplies. The results are also complicated by variations in the initial and final moisture distributions in the subsoil (Marshall and Stirk, 1950). Advances in the techniques for taking and for handling of soil cores, made in recent years by workers in the U.S.A., have rendered practical their use in large-scale field experiments. By the method described below, behaviour of the soil surface under rainfall impact may be observed on soil of undisturbed pore-space. In addition the standard measurements of pore-space and percolation may be made as required. Only simple laboratory equipment is needed, and the method has been found practical for routine sampling on field experiments.

Details of Method

Undisturbed soil cores 4 in. in diameter and 3 in. deep are taken from the soil surface by a sleeved hammer-driven sampling cylinder (Pereira, 1954). The sleeves are standard commercial tinplate cans with slip-on lids at both ends. After replacement of the lower lids by fine cotton cloths, secured by rubber bands, the cores are wetted in large vacuum desiccators, in which pressure is reduced to $\frac{1}{4}$ atmosphere in order to facilitate the escape of entrapped air. The cores rest on the stage of a desiccator fitted with inlets for both water and air. After reduction of air pressure the water-level is raised to 1 cm. above the stage, and maintained there while the cores are wetted by capillary rise. After 30 min. the water-level is raised to within 1 cm. of the tops of the cores. After a further 30 min. air is admitted and the water run out. The cores are then drained for 24 hours at a tension of 20 cm. of water on tension tables built to the design of Jamison and Reed (1949). For use in East

Africa in the dry season the tension tables are enclosed in a glass cabinet to reduce evaporation. The cores are then weighed rapidly to the nearest gramme and placed in turn in the apparatus shown in Plate I. The core rests on a diaphragm consisting of three sheets of filter paper (Whatman No. 5) in a Buchner funnel. For convenience a 6-in. funnel is used, the outer holes in the perforated base being sealed. A tension of 20 cm. of water is applied by connecting the filter flask to a large vacuum

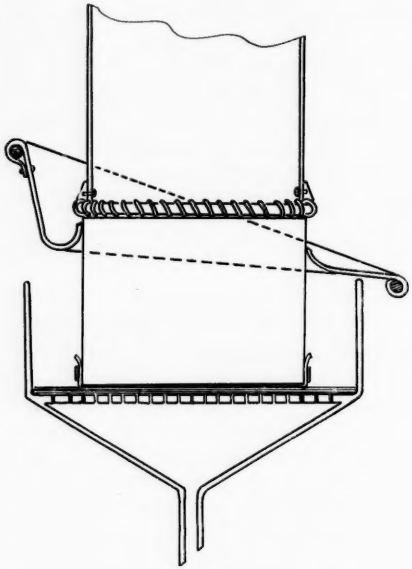

FIG. 1

desiccator, from which air is withdrawn by a filter pump. Suction is regulated by admitting air to the desiccator from a submerged inlet (Plate I).

Around the top of the core is placed a pear-shaped rubber tray cut from heavy rubber sheet (tractor-tyre inner tube), shown in section in Fig. 1. This tray has a central hole of $3\frac{1}{2}$ in. diameter, so that the rubber is stretched to give a water-tight joint around the 4-in. core sleeve. The edges of the rubber tray are supported by a stiff wire frame, and the tray is tilted so that any water which it may collect will be delivered through the spout formed by the narrow end.

The upper lid of the core-container, which has been retained to this stage in order to minimize the risk of distortion of the core by handling, is now removed, and a spirit level is used to verify that the soil surface is horizontal. A cast-iron retort-ring of 4 in. internal diameter is then clamped firmly on the upper edge of the core-sleeve. This ring is bound with wire of 14 s.w.g., the turns being spaced $\frac{1}{4}$ in. apart. The internal diameter of the wire-wound ring is thus reduced so that the 4-in.

diameter core-sleeves are firmly centred and held in position (Fig. 1). A cylinder of transparent 'perspex', or a metal cylinder with a transparent window, is mounted on the upper side of the ring to form a splash-shield. All splash is returned to the soil surface, since unit area of a horizontal soil surface may be assumed to receive as much splash from surrounding areas as it loses to them. When the infiltration-rate is less than the rate of application, the excess water flows over the edge of the sleeve, through the apertures between the turns of wire, and is caught by the rubber tray. A filter paper collects the larger particles of transported soil as the run-off water is discharged into a filter flask connected to a second filter pump. The apparatus stands on a metal tray which is slid under the rainfall simulator. A clock is started at the same time, and the apparatus is removed after 10 min. The drainage tension is maintained for a further 5 minutes.

The volume of run-off in the filter flask is measured. The filter funnel is then replaced and any soil particles observed on the rubber tray are washed on to the filter. The small quantity of transported soil is then returned to the surface of the soil core, which is rapidly weighed on a direct reading balance. The volume of water drained from the core is next measured. A 5-min. check on the rate of delivery by the rainfall simulator may conveniently be made while the core is weighed and the volumes of water are measured. With one operator the test requires 30 min. per core.

The water accepted by the soil surface is the sum of the drainage volume and of the change in storage (from change in weight) of the soil core. Addition of the volume of run-off gives the total quantity of water received. The results may be expressed as rate of rainfall acceptance, as water accepted per cent. of water applied, or perhaps most appropriately as inches of water accepted from the 1-in. test 'storm'.

Simulation of Heavy Rainfall

Ellison (1944, 1952) has shown that the greatest erosion damage is caused by the impact of raindrops having the highest energy. Raindrops of 5 mm. diameter require about 20 metres to reach terminal velocity in still air, so that the direct reproduction of such maximum raindrop energy in the laboratory is not convenient. It is fortunately not necessary for this type of soil test, since much lower raindrop energies cause severe surface damage, while varying conditions of wind and weather produce a wide range in the actual size and energy of raindrops. Provided that the drop-size and energy can be standardized, the severity of the test may be adjusted by the duration and intensity of the 'storm' applied. For convenience in laboratory measurements on large numbers of cores it is most desirable that the operations should be at bench level. In order to leave space for the necessary apparatus a fall of 2 metres has been used. The large drops employed attain over 50 per cent. of their terminal velocity in this distance.

Bean and Wells (1953) quote Blanchard's finding that elongation due to air resistance limits the maximum diameter of stable raindrops at

terminal velocity to 5·4 mm. Larger drops can be used for shorter falls, but a diameter of 6 mm. was selected for these tests as near to the maximum observed in the field during storms. The duration and intensity were chosen to test the most erosion-resistant lateritic clay, in its optimum condition when newly broken from long-established elephant grass. The extremely severe application of 1 in. of water in 10 min.

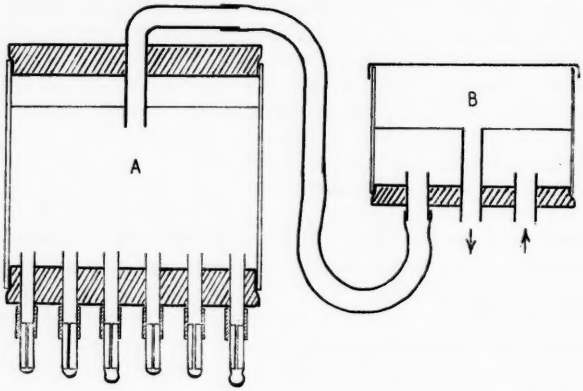

FIG. 2

was found necessary in order to produce a slight run-off. The same soil when over-cultivated accepted only two-thirds of this application, while a sandy loam very prone to capping accepted only 40 per cent. The rate is therefore appropriate to the East African soil types so far tested. A less severe application would be advisable for soils of very low stability.

The production of waterdrops of a uniform size at a uniform rate may be achieved in many ways. The apparatus shown in Fig. 2 requires only simple and inexpensive laboratory materials. The short sections of glass capillary tubing are readily detached for cleaning. When the apparatus is not in use these jets should be washed in distilled water, dried, and stored away from dust. The vessel *A* is conveniently made from a spare pressure-lamp glass. By closing it at the top the control of flow rate by the levelling vessel *B* is considerably improved. The latter is carried on a vertical supporting rod adjustable from the bench, as shown in Plate I. Ten jets are used; these are 2-cm. lengths of thick-walled capillary tubing of 0·4 mm. bore and 6·0 mm. external diameter. The level in *B* is usually set below the level in *A* with these jets. The temperature of the overflow from *B* is observed at bench level. When the laboratory cistern is of sufficient capacity to supply water within a temperature range of approximately $\pm 2^{\circ}$ C. no closer control is required. If, however, the temperature of the laboratory supply is found to fluctuate widely, regulation through a constant-temperature water bath is preferable to frequent adjustments of flow rate.

Examples of Results from Rainfall Test

A complex long-term rotation experiment was laid down by the Uganda Department of Agriculture in 1936 at the Serere Agricultural Station (Martin and Biggs, 1937). The soil is a compact sandy loam with little visible structure and much surface capping. Mechanical analysis of the first 6 in. of soil gives approximately 15 per cent. coarse sand, 50 per cent. fine sand, 15 per cent. silt, and 20 per cent. clay. The mean annual rainfall is 54 in., with a severe dry season.

In January 1954 the experiment was sampled to study structural differences resulting from three different 5-year rotations after 15 years of operation. The rotations contained respectively 1-, 2-, and 3-year planted grass leys, all both with and without grazing. Two soil cores per plot were taken from 36 plots. One-third of the plots were under grass awaiting the plough at the end of the ley period; one-third were under cotton at the end of the first year of the arable break; the remainder were in their second year of arable after grass. Much termite activity was observed, including species of soil-eating termites, and it was necessary to treat all cores with insecticide to guard against effects of insects accidentally included in the soil.

Measurements on each of the 72 cores included total pore-space, pore-space drained at 20 cm. and at $\frac{1}{3}$ atmosphere, percolation rate under 1 cm. head of water (all by techniques described elsewhere (Pereira, 1954)), and finally the artificial-rainfall test described above. Table 1 summarizes the results of the three most effective tests, for the three principal rotation contrasts.

TABLE 1

Average Effects of Length of Grass Rest in a 5-year Rotation

(Each figure is the mean value of 24 soil cores)

	One year of grass	*Two years of grass*	*Three years of grass*	*Standard error per sample*	*Coefficient of variation*	*Significances of differences*
	g_1	g_2	g_3		%	
Freely drained pore-space as percent. total soil volume . .	12·7	12·4	13·8	±3·1	24	Nil
Percolation rate in inches per hour . .	4·5	5·5	13·0	±8·4	110	$g_3 > g_2$ and g_1 at $P = 0{\cdot}001$
Rainfall acceptance in inches from 1 in. per 10 min. . .	0·35	0·43	0·45	±0·13	31	$g_3 > g_1$ at $P = 0{\cdot}01$ $g_2 > g_1$ at $P = 0{\cdot}05$

The freely drained pore-space is a useful direct measurement of an important property, but this test has failed to establish differences between the rotations at the 5 per cent. level of statistical significance. The percolation rates are governed by the continuity and orientation of insect burrows, as well as by the volume of pore-space. They are

therefore highly variable. The very significant increase due to the 3-year grass rest is due largely to the observed higher termite populations associated with the larger volume of herbage and the shorter arable break.

A major physical disadvantage of this soil type is the capping of the surface by rainfall. This is illustrated by the low rainfall acceptance figures in Table 1. Although cores taken at the end of 3 years of grass accepted 60 per cent. of the severe 1-in. test 'storm', the average for this rotation was only 45 per cent. and that for the experiment was only 41 per cent. A significant improvement in this critical property of the soil surface was achieved by both additional years of grass rest.

Comparisons with wet- and dry-sieving tests in addition to those with pore-space and percolation measurements are reported elsewhere for a large-scale tillage trial in Kenya coffee (Pereira and Jones, 1954) and for another rotation experiment in Uganda cotton (Pereira, Chenery, and Mills, 1954). From the comparative results of the several criteria used we can only conclude that no single test yet devised will give us comprehensive information on the structural condition of a soil. The rainfall test described here adds to our information on a soil property which is of practical field importance in many climates and is of major importance in East African conditions.

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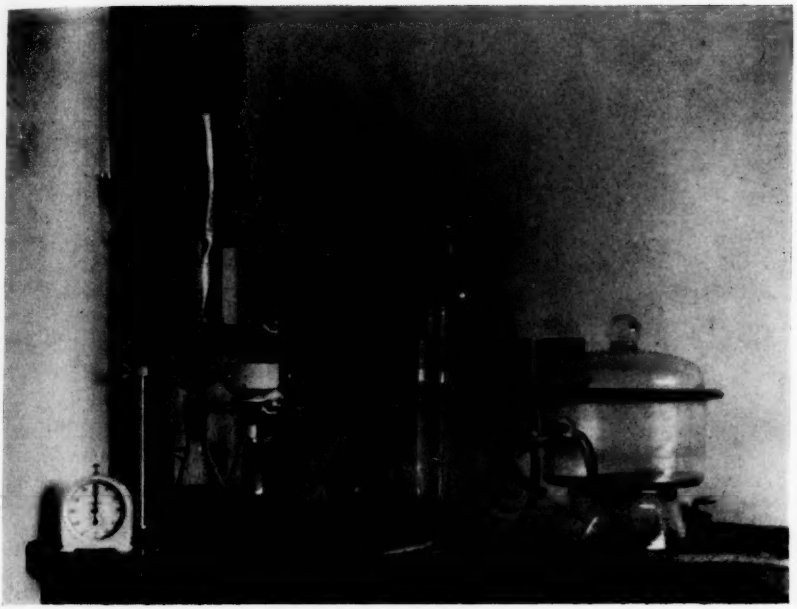

H. C. PEREIRA—PLATE I

STRUCTURAL CHANGES DURING BULK SOIL STORAGE

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WHEN opencast coal sites in Northumberland and Durham began to be returned to agricultural use, it was immediately apparent, on the heavier boulder clay soils, that a marked change had occurred in their working characteristics.

Field inspection gave the following indications of deterioration in soil structure:

1. Poaching by animals and machines was more marked.
2. Tilth was more difficult to obtain and was of the harsh mechanical type which collapsed in heavy rain.
3. On steeper slopes surface erosion occurred, with gullying to a depth of 3 ft. in some cases.
4. Shallow rooting and marked nitrogen deficiencies were common in many crops. Areas receiving dung or generous fertilizer treatment stood out in sharp contrast.
5. In dry weather cracking was extensive with strikingly better growth along the sides of the cracks due to improved aeration.
6. Earthworm activity was negligible.

Fertilizer Response

Field and pot experiments were laid down to assess crop response to fertilizer treatment. Consistently it was found that:

1. pH levels were satisfactory.
2. A 'starter' dressing of phosphate was essential. 3 cwt. per acre of superphosphate or its equivalent was adequate. Thereafter annual phosphate requirements were even more modest.
3. No response was obtained to potash.
4. The requirement of available nitrogen was extremely high and was the critical factor in most cases. Residual effects from nitrogen dressings were very small indeed.

Soil Structure

Soil structure was examined in the laboratory by modifications of the methods of Alderfer and Merkle (1941) and Chizhevsky and Baksheev (1947) for water-stable aggregates. Air-dry soils, lightly ground to pass a 4-mm. sieve, were used. After 24 hours' preliminary soaking 'clay'- and 'silt'-sized fractions were determined by sedimentation and pipette sampling. Fractions larger than 0·2 mm. were then separated by wet-sieving over a series of oscillating sieves in static water.

The 'dispersion ratio' defined by Middleton (1930) as:

$$\frac{(\text{clay}+\text{silt in the undispersed soil}) \times 100}{\text{clay}+\text{silt in mechanical analysis}}$$

appeared to be the best single-value constant to indicate soil structure. Development of macrostructure was discarded as a criterion because it did not always correspond with a return of the original working characteristics. This was usually due to an increased amount of unaggregated material less than 0·2 mm. in diameter. Dispersion ratio seemed to correlate well with root development, permeability, and increase in electrical conductivity after 7 days' incubation. It also corresponded with response to fertilizer nitrogen and friability of tilth. It will be noted in Table 1 that worked soils invariably had a higher dispersion ratio.

TABLE 1

Water-stable Soil Aggregates

BLAGDON

	Worked		*Unworked*	
Depth	*% particles 0·2 mm.*	*Dispersion ratio*	*% particles 0·2 mm.*	*Dispersion ratio*
0–3 in.	53·3	22·1	60·4	10·9
3–6 in.	18·1	37·6	67·5	8·7
6–9 in.	16·0	43·7	62·3	11·1

MILKHOPE

	Worked		*Unworked*	
Depth	*% particles 0·2 mm.*	*Dispersion ratio*	*% particles 0·2 mm.*	*Dispersion ratio*
0–3 in.	30·6	28·0	46·9	12·9
3–6 in.	37·0	26·6	44·8	11·9
6–9 in.	37·4	24·6	48·2	13·2

Porosity was measured by taking clods 3–4 cm. in diameter direct from the field at field moisture content and quickly transferring them to the laboratory in air-tight waxed paper cartons. Each clod was gently brushed to remove loose particles, weighed and lightly coated by immersion in paraffin wax (m.-pt. 45°) at 50° C. The volume was found by weighing in air and in water. Finally the wax covering was removed and the moisture content of the soil determined.

Table 2 shows the marked decrease in porosity after working.

Permeability

Permeability of undisturbed cores and of cores artificially packed in the laboratory was measured with apparatus similar to that of Bloodworth and Cowley (1951). The artificial cores were prepared from air-dry soil, ground to pass a 2-mm. sieve, and after packing were slaked *in vacuo*. The greater permeability of unworked soils is shown in Table 3.

TABLE 2

Soil Porosity

BLAGDON

Depth	*Worked*		*Unworked*	
	Total porosity % of volume	*Volume weight (g./c.c.)*	*Total porosity % of volume*	*Volume weight (g./c.c.)*
0–3 in.	32·78	1·581	50·14	1·149
3–6 in.	36·41	1·638	49·69	1·153
6–9 in.	35·32	1·622	52·68	1·117

TABLE 3

Permeability (in./hour)

BLAGDON

Depth	*Worked*		*Unworked*	
	Artificial	*Undisturbed*	*Artificial*	*Undisturbed*
0–3 in.	0·115	0·003	1·74	0·25
3–6 in.	0·046	0·160	3·12	2·03
6–9 in.	0·027	0·004	0·87	0·62

Possible Causes of Structural Deterioration

There is, therefore, considerable evidence that deterioration of soil structure has occurred as a result of opencast coal working. Three possible causes have been considered:

1. Admixture of subsoil and loss of topsoil.
2. Mechanical manipulation under unfavourable moisture conditions.
3. Loss of organic matter.

On some of the earlier sites there is no doubt that the first factor did apply and, largely due to lack of experience, topsoil was sometimes buried or mixed with subsoil. As time went on restoration technique improved greatly and recently both topsoil and subsoil layers have been replaced with considerable skill. A high standard of replacement must be maintained, but even so the symptoms of damage to structure still remain.

The second factor obviously is of some consequence because most soil manipulation must, of necessity, be done at moisture contents above the lower plastic limit. It has not been possible to explore fully this effect, but since structural breakdown has been produced in the absence of mechanical manipulation it may well be that plastic deformation contributes to loss of structure by intensifying the anaerobic condition and thereby increasing the effect of the third factor.

Without doubt some organic matter is destroyed in topsoil heaps. On opening, the characteristic anaerobic smell is immediately detected. Compared with unworked soil there was an increase in the plasticity number similar to that obtained when the original soil is treated with

6 per cent. hydrogen peroxide. Moreover, the character of the organic matter in worked and unworked soils seems to be quite different. Replicate 1-g. samples of both soils were treated with increasing amounts of 6 per cent. hydrogen peroxide and the organic carbon remaining in the soil after this treatment was determined by the chromic-acid-oxidation method of Walkley and Black (1935). The results for Milkhope soil in Table 4 show that not only does the worked soil contain less organic carbon, but the character of the organic matter in worked soil is very different from that of the original soil. The latter is rapidly attacked by hydrogen peroxide and a state of equilibrium is soon reached. In contrast, the organic matter of the worked soil is not so readily attacked and reaches equilibrium much more gradually. It seems reasonable to assume that some of the organic matter intimately concerned in aggregation of silt and clay has been either broken down or converted into less active forms. An attempt has been made to reproduce this effect in the laboratory.

TABLE 4

Breakdown of Organic Carbon

Comparison of Worked and Unworked Soils (Milkhope)

6% H_2O_2 *added* (*ml.*)	*Unworked*		*Worked*	
	% *organic carbon in soil*	% *of original*	% *organic carbon in soil*	% *of original*
0	1·98	10·0	1·89	10·0
2	..	..	1·89	10·0
4	0·54	27·3	..	..
6	..	..	1·11	58·7
8	0·42	21·2	0·87	46·0
10	0·33	16·7	0·78	41·3
12	0·31	15·9	0·66	34·9
14	0·31	15·9	0·66	34·9
16	0·31	15·9	0·63	33·3
18	0·31	15·9	0·58	30·9
20	0·31	15·9	0·55	29·4

Anaerobic Incubation of Soil

Samples of unworked air-dry topsoil were prepared by sieving off the 1–2-mm. and 2–4-mm. crumbs. 50-g. samples were placed in screw-top jars of some 60-ml. capacity. Moisture content was maintained at 30 per cent. and the samples were incubated at 20° C.—half being sealed and the others remaining open. At intervals during succeeding weeks parallel pairs of samples were removed and the structure examined by the methods already cited.

On opening the anaerobic samples the smell indicated some degree of bacterial decomposition. Furthermore, during the pipette analysis, suspensions of the anaerobic samples gave distinctly opalescent suspensions in contrast to the clear suspension of the aerobic soils. As the period of incubation progressed the extract from the anaerobic samples

became increasingly brown. The dispersion ratios of the two series of samples given in Table 5 show consistently higher figures for the anaerobic samples. There is, however, no relation between time of incubation and dispersion ratio.

TABLE 5

The Effect of Incubation at 20° C. on Structural Stability

	Incubation period (weeks)	*Dispersion ratio*	
		Aerobic	*Anaerobic*
BLAGDON SOIL (1–2 mm.)	2	2·24	3·72
	4	3·55	5·27
	6	1·76	3·76
	16	2·01	4·56
	Mean	2·39	4·33
BLAGDON SOIL (2–4 mm.)	2	1·71	3·97
	4	3·16	4·24
	6	3·55	4·12
	16	2·05	4·01
	Mean	2·62	4·09
MILKHOPE SOIL (2–4 mm.)	4	8·17	9·81
	8	7·47	7·74
	12	9·04	10·71
	20	4·97	9·54
	Mean	7·41	9·45

In a further experiment similar incubation was carried out with soils pretreated with one of the new hydrolysed polyacrylonitrile soil conditioners. These soils proved to be much more resistant to anaerobic breakdown. It is not suggested, however, that this is a solution to the problem because such treatment would be quite uneconomic. Indeed, if this breakdown mechanism is confirmed, it seems that some structural deterioration in the soil is an inevitable result of opencast coal working. Future research may most profitably be directed to a study of agricultural practices which will most quickly restore structure to its initial level.

Summary

Field and laboratory evidence has been presented to show that opencast coal working on the heavier boulder clay soils in Northumberland and Durham causes some deterioration in physical structure.

It is suggested that anaerobic conditions in the topsoil heaps have affected organic compounds concerned in soil aggregation.

Under the present system of working, damage to structure is probably inevitable.

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ELECTRON-MICROSCOPE OBSERVATIONS OF THE REACTION OF PHOSPHATE WITH MINERALS, LEADING TO A UNIFIED THEORY OF PHOSPHATE FIXATION IN SOILS

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WITH THREE PLATES

Introduction

A NUMBER of crystalline phosphates have been shown to result from the phosphate treatment of various clays and hydrous oxides at 95° C. (Haseman *et al.*, 1950). By means of the electron microscope, the mechanism of solution-precipitation has been shown to be important in the phosphate reaction with kaolinite at 90° C. (Kittrick and Jackson, 1954). This mechanism is also operative in the reaction of phosphate with colloidal iron oxide particles and thin aluminium hydroxide films at room temperature (Kittrick and Jackson, 1955*a*).

It is the purpose of this paper, first, to compare the reaction of phosphate with the iron silicate greenalite* at 90° C. with the previously reported reaction of phosphate with kaolinite at that temperature; second, to show that phosphate also reacts with the minerals greenalite and kaolinite at room temperature to form new separate phases; and third, to show that 'surface phosphate' can be a part of a colloidal separate phase. These considerations make possible the formulation of a unified theory of phosphate fixation in soils through a reaction mechanism that can be applied to soil-phosphate systems in general.

Experimental

The minerals employed were greenalite (2–5 μ) from Gilbert, Minnesota, and kaolinite (−2 mm.) from the McNamee mine near Langley, South Carolina. One-tenth-gramme samples of greenalite and kaolinite were treated with 15 ml. of one molar sodium and potassium phosphates, and pH adjustments were made with NaOH and KOH, respectively for the corresponding salt. Some of the greenalite samples were placed on the steam hotplate (about 90° C.) to hasten the reactions. At suitable time intervals each sample was washed five times with distilled water by the centrifuge technique, and then a portion of the sample was removed for electron microscope examination. The remainder of the sample was treated with a fresh phosphate solution of the same composition as before. Upon completion of the experiment, the remainder of the sample was washed five times with distilled water and once with acetone by the centrifuge technique, dried, and X-rayed by the powder method.

* The exact structure of greenalite is not known, but it is thought to be the iron analogue of kaolinite and antigorite.

Results

Reaction mechanism. Considering first the reaction of phosphate with greenalite at 90° C., the rapid dissolution of the greenalite was observed (notice the partially decomposed greenalite crystal in Plate I B) concurrent with the formation of the new phosphate phase (Table 1). This reaction mechanism is identical to the one dominating the reaction of phosphate with kaolinite systems at 90° C. (Kittrick and Jackson, 1954). That the reaction mechanism of phosphate with kaolinite and greenalite at room temperature is also solution-precipitation is shown in Plates II and III. Here again the familiar sequence was observed of the dissolution of the iron or aluminium source minerals (particularly Plates II B and III B) concurrent with the formation of the new phosphate phase.

Reaction rate. Since the reaction mechanism in all systems is solution-precipitation, the most striking difference between these systems is one of reaction rate. The colloidal iron oxide particles and thin aluminium hydroxide films react with phosphate at room temperature to form phosphate precipitates which are readily observable with the electron microscope a few *minutes* after treatment (Kittrick and Jackson, 1955*a*). To reach the same stage in the kaolinite and greenalite systems at 90° C. requires a few *days*, while a few *years* are required for similar results in the kaolinite and greenalite systems at room temperature.

A number of workers have found that the fixation of phosphate by soil minerals is characterized by two stages, an initial rapid reaction which quickly diminishes to a much slower reaction that apparently continues indefinitely (Wild, 1950). Haseman *et al.* (1950) working with iron and aluminium minerals reasoned that the high initial reaction of phosphate was with more 'readily available' aluminium and iron (high specific surface sources of aluminium and iron such as represented by the colloidal iron oxide and aluminium hydroxide films, Kittrick and Jackson, 1955*a*) while the subsequent slower reaction of phosphate was with ions released by concurrent decomposition of the soil minerals (as illustrated by Plates I, II, and III herein). The authors feel that the electron micrographs of crystals formed at room temperature graphically illustrate the correctness of both portions of this hypothesis.

If one were to attempt to repeat these room-temperature experiments with kaolinite and greenalite, observing the systems only with the ordinary light microscope, after several years of observation one would probably conclude that phosphate precipitates do not form in these systems, even though they are clearly visible with the electron microscope. Were a microscope available that was even more powerful than the electron microscope, one probably could observe the formation of these phosphate particles after only a few days' contact between soil mineral and phosphate solution at room temperature. It is probable, then, that these phosphate particles form immediately upon phosphate treatment of kaolinite and greenalite, but initially are very small with tremendous surface area; it requires about 2 years before they grow large enough to be seen easily with the electron microscope, and to become sufficiently numerous to prevent their classification as artifacts.

With colloidal iron oxide and aluminium hydroxide systems, the new phosphate particles were observed to form within a few minutes (Kittrick and Jackson, 1955*a*).

Reaction products. In the high-temperature systems where rapid crystal formation took place, X-ray diffraction analysis of the reaction products was a simple matter, since the new crystal phase made up a substantial percentage of the total crystalline material present; however, chemical analyses were not performed on these systems since considerable unreacted kaolinite and greenalite remained.

The electron microscope can be much more sensitive than X-ray diffraction to the formation of new phases, and the new phases formed in Plates II and III can be easily distinguished from the controls. The only new phase identified by X-ray diffraction in the room temperature experiments was taranakite in the potassium phosphate-kaolinite system (Plate III B). The other new phases were either not sufficiently crystalline or were not abundant enough to produce X-ray diffraction lines that could be delineated from the strong patterns of the unreacted kaolinite or greenalite.

It is interesting to note that while the potassium phosphate-kaolinite system formed taranakite at room temperature, this same system formed minyulite at 90° C. (Table 1), therefore the resultant crystal phase in this case is a function of temperature. It can be seen from Table 1 that the reaction products were sometimes a function of pH and always were a function of the cation present. Since the reaction products seem to be so dependent upon experimental conditions, it is probable that in the soil system several insoluble phosphate species are formed, in different micro-environments near different soil mineral particles.

TABLE 1

New Phosphate Phases resulting from the Phosphate Treatment of Kaolinite and Greenalite at 90° C.

(The approximate formulas given are calculated from the analysis performed by the workers cited)

Original mineral	*One molar phosphate treatment at 90° to 100° C.*		*New phosphate phase identified by X-ray analysis*	*Approximate formula of new phosphate phase*
Kaolinite, $Al_2(Si_2O_5)OH_4$	KH_2PO_4	pH 4·3	Minyulite-like‡	$KOH(Al)_2(PO_4)_2 \cdot 2H_2O$
		pH 7·0	Product J†	$KOH(Al)_2(PO_4)_2 \cdot 2H_2O$
	NaH_2PO_4	pH 4·3	Product 12*	$(H, Na)_3Al_2(PO_4)_2 \cdot 3H_2O$
		pH 7·0	Product G†	..
Greenalite, possibly $Fe_2(Si_2O_5)OH_4$	KH_2PO_4	pH 4·3	Product I†	$KOH(Fe)_2(PO_4)_2 \cdot 2H_2O$
		pH 7·0	Product I†	$KOH(Fe)_2(PO_4)_2 \cdot 2H_2O$
	NaH_2PO_4	pH 4·3	Product 16	(See Table 2)
		pH 7·0	Product 17	(See Table 2)

* Haseman *et al.*, 1950.
† Haseman *et al.*, 1951.
‡ Kittrick and Jackson, 1954.

TABLE 2

X-ray Diffraction Data for the New Phosphate Phases resulting from the Reaction of Greenalite at 90° C. with NaH_2PO_4 *at pH 4·3 and pH 7·0*

(All possible lines due to greenalite have been omitted)

*Product 16** *pH 4·3*		*Product 17* *pH 7·0*	
d/n	*Intensity*	*d/n*	*Intensity*
11·0	S	11·0	M
10·1	M	10·0	M
		6·26	W
6·16	W	6·09	W
5·52	M	5·58	M
5·34	M	5·29	S
5·05	W		
4·74	W	4·70	M
		3·49	W
3·16	W	3·21	W
3·10	W	3·08	M
		3·04	W
		2·93	W
		2·87	W
2·77	M	2·75	S
		2·72	M
2·67	M	2·68	M

* It is common in the literature to see phosphate X-ray diffraction patterns as similar as those of products 16 and 17, suggesting that a few basic phosphate structures exist which are modified by isomorphous substitution and other factors.

A Unified Theory of Phosphate Reaction Mechanism

Usually science progresses by inductive reasoning from observed facts to theories or principles, then through deductive reasoning, predicts expected new facts. Where several theories attempt to describe the same phenomena, the one that best explains the most of the observed facts is generally accepted and should be the most useful in predicting results not yet observed through experimentation.

Experimental measurements of the reaction of phosphate with soil minerals vary considerably depending on the particular range of experimental conditions employed. This variation has led to the development of several reaction mechanism theories, some of which can explain the observed facts only in a limited range of experimental situations. It would be highly desirable if one theory of the reaction mechanism could be formulated that would hold through the whole range of observations of the reaction of phosphate with soil minerals, through both initial and subsequent reactions, for example. Such a theory may be termed 'a unified theory' for reaction mechanism if it relates all experimental observations satisfactorily. The authors propose that such a unified theory can be formulated, based on the formation and growth of separate

phases of varying specific surface, precipitated by ions from solution or at the surface of mineral particles.

Through the years three main phosphate fixation theories have been developed; they are isomorphous substitution, adsorption, and chemical precipitation.

Isomorphous substitution. The theory of large scale substitution of P for Si in tetrahedral structural units in soil silicate minerals has been refutated experimentally (Bauwin and Tyner, 1954) by the extraction with $Na_2S_2O_4$ reduction-chelation of the formerly called 'non-extractable' soil phosphates which had previously been postulated to be tetrahedral in silicates. This extraction treatment dissolves iron oxide coatings, and would also be expected to dissolve iron phosphate. The theoretical replacement of PO_4 for OH in a crystal structure is unlikely, since the phosphate tetrahedron is several times too large to occupy a hydroxyl site. Thus isomorphous substitution, either P for Si or PO_4 for OH, is a mechanism which is neither wholly tenable nor of general applicability. Positive surface charges, possibly neutralized by hydroxyl, do exist in soils (Russell, 1950) associated with edges of layer silicate clay particles and with iron and aluminium compounds, and this hydroxyl might exchange for phosphate; however, such surface phenomena can best be considered as an adsorption mechanism.

Adsorption. Adsorption of phosphate refers to the process of concentration at surfaces of a solid phase of phosphate ions from solution in forms that are exchangeable or replaceable. It is known that so-called 'adsorption isotherms' are not specific as to reaction mechanism and fit the process of chemical precipitation (Fisher, 1922; Boyd *et al.*, 1947) as well as physical adsorption. Adsorption as usually applied to phosphate reactions in soils has the temperature sensitivity characteristics of chemical reactions. The theory of adsorption can be satisfactorily applied only in the domain of initial reactions between phosphate and soil minerals. A different theory, involving formation of phosphate precipitates (multiple layers, &c.), generally has been postulated to explain later events such as the decrease in exchangeability or availability with time and direct observations of phosphate crystals. Adsorption thus does not provide the general principle sought.

Chemical precipitation. Chemical precipitation of phosphate refers to the removal of phosphate ions from solution and their chemical bonding to the solid phase. The solid phase formed may be as monolayer additions on the surface of a solid phase of the same kind (crystal growth) or addition to a second solid phase (chemisorption). It may also be in the form of new particles. This definition of chemical precipitation includes that part of adsorption which involves chemical reactions. The rate of reaction of phosphate with soil minerals increases with increase in temperature (Haseman *et al.*, 1950; Low and Black, 1950), both during the initial rapid reaction and during the subsequent slower reaction, indicating that chemical forces (Glasstone, 1946) are involved at both reaction rates. The electron microscope observations of the formation of separate phosphate phases *at room temperature* both from slow reactions with minerals (Plates II and III) and from fast reactions with

thin oxide films (Kittrick and Jackson, 1955*a*) supports the concept of a single (unified) theory based on a chemical precipitation mechanism as the general case.

To be generally applicable, the unified theory, based on chemical precipitation, should be consistent with phosphate specific surface data. Olsen (1952) showed that P^{32} exchangeability is essentially a measure of

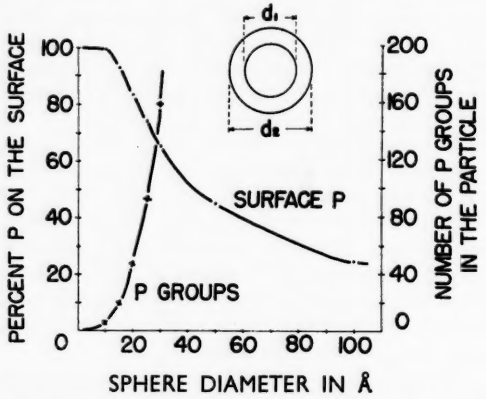

FIG. 1. Variation in the percentage of phosphate groups on the surface of spherical apatite particles (density 3·16 g./cm.^{3}). Using 4·45 Å as the depth of a phosphate group (Olsen, 1952), $d_2 - d_1 = 8{\cdot}90$ Å. The percentage surface phosphate was calculated by division of the volume difference between sphere d_1 and sphere d_2 by the volume of sphere d_2, times 100. By this method of calculation a sample of apatite reported by Cole *et al.* (1953) to have 58 M^2/g. specific surface and 8 per cent. of its phosphate replaceable by P^{32}, was calculated to have 8·6 per cent. of its phosphate on the particle surface. The measured 8 per cent. and calculated 8·6 per cent. are in excellent agreement.

surface phosphate. In calcium systems, Cole *et al.* (1953) found that phosphate applied to calcium carbonate in very dilute solutions was initially almost completely exchangeable with P^{32}, and with time became more and more incompletely exchangeable. The amount of P^{32} exchangeable phosphate in freshly precipitated iron and aluminium phosphates also decreases with time (personal communication from M. Fried, U.S. Dept. of Agriculture, by permission).

The percentage of phosphate on the surface of varying particle sizes of calcium phosphate and aluminium and iron phosphate was calculated. In the calculation of the expected variation in per cent. surface phosphate with particle size, spherical particles seem to be a good approximation for apatite. It can be seen from Fig. 1 that spherical apatite particles 15 Å in diameter would contain about 20 phosphate groups, over 93 per cent. of which would be on the particle surface. Even more important than particle size in determining per cent. surface phosphate is particle shape. For example, a platy particle similar to those formed when thin films of aluminium hydroxide are treated with 1 *M* KH_2PO_4 at pH 7 for 120 min. at room temperature (Kittrick and Jackson, 1955*a*) has a

length : width : depth ratio of approximately 50 : 25 : 1. Thin flat particles smaller than 500 Å in long dimension were observed. Following the procedure of Olsen (1952), the equivalent approximate depth of a phosphate group calculated as the side of a cube is 4·5 Å in apatite, is 4·7 Å in variscite ($AlPO_4.2H_2O$), and is 4·8 Å in strengite ($FePO_4.2H_2O$). Assuming 5 Å to be a rough approximation of the depth of a phosphate group in many phosphate minerals, a phosphate particle 500 Å × 250 Å × 10 Å would have all its phosphate groups on the surface where they could be replaced with P^{32}. The degree of exchangeability would depend on the shortest dimension of the particle. Obviously in any collection of phosphate particles there will be some gradation in particle thickness; some particles will be thin enough for complete P^{32} exchangeability and others less so.

The decrease in phosphate surface area of calcium, iron, or aluminium phosphates generally observed with time can be interpreted simply as an increase in particle size with time, the process being driven by an exothermic decrease in surface energy. Since surface phosphate has been well correlated with crop response, this exothermic increase in particle size readily explains the decrease in availability and P^{32} exchangeability of applied fertilizer phosphorus with time, all within the unified theory of phosphate reaction mechanism based on chemical precipitation.

The origin, composition, and stability of the phosphate phase formed is regulated by the solubility product principle as applied to soil systems by Cole and Jackson (1951) and Kittrick and Jackson (1955*b* and 1955*c*). The initial composition of these new phosphate phases depends on the predominant cations present on a microscale, and the particles of the new phases increase in size with time.

It is clear then that the formation and growth of chemically precipitated phosphate phases is in accord with the observed facts of phosphate reaction with soil minerals, not only after long periods of contact, but also during initial surface phosphate exchange reactions as well.

Summary

It has been shown that greenalite and kaolinite react with phosphate by the mechanism of chemical precipitation to form separate-phase phosphate crystals at room temperature as well as at 90° C. The species of crystalline phosphates formed was found to depend upon the experimental conditions, the room-temperature systems requiring a longer time to reach the observational stage. The specific surface of phosphate precipitates was calculated from particle size and shape, and the surface area of precipitated phases was found to be sufficient to account for 100 per cent. P^{32} exchangeable phosphate and less, according to particle shape and size. The presence of separate-phase phosphate precipitates was found to be consistent with the observed facts of phosphate reaction with soil minerals, both initially and subsequently.

It is suggested that the formation and growth of separate-phase phosphate precipitates of varying composition, depending on the predominant cations, and of varying reactivity depending on specific surface, formed by the mechanism of chemical-precipitation, whose chemistry is

controlled by solubility product principles, provides a unified theory of phosphate fixation which explains the whole range of observed facts of phosphate reactions in iron, aluminium, and calcium soil systems.

Acknowledgements

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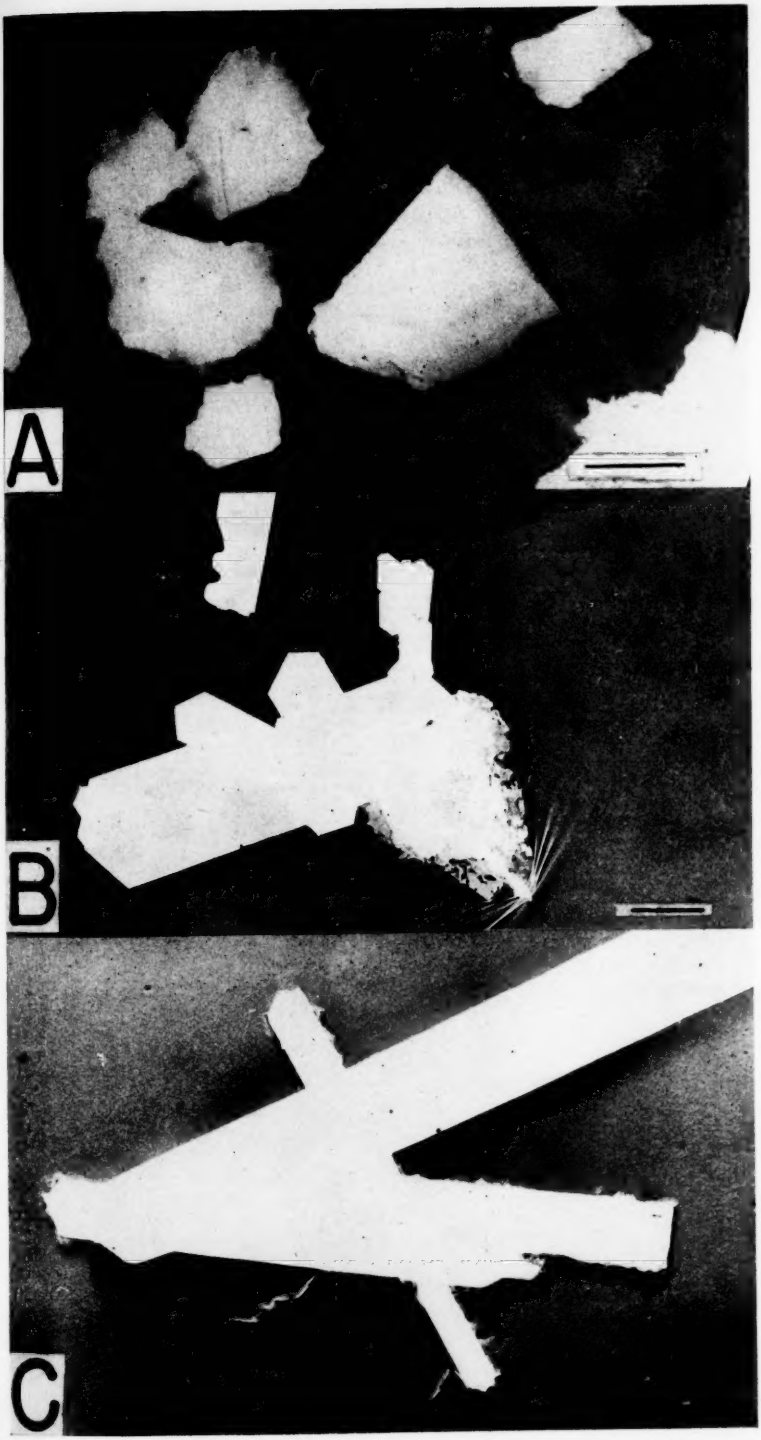
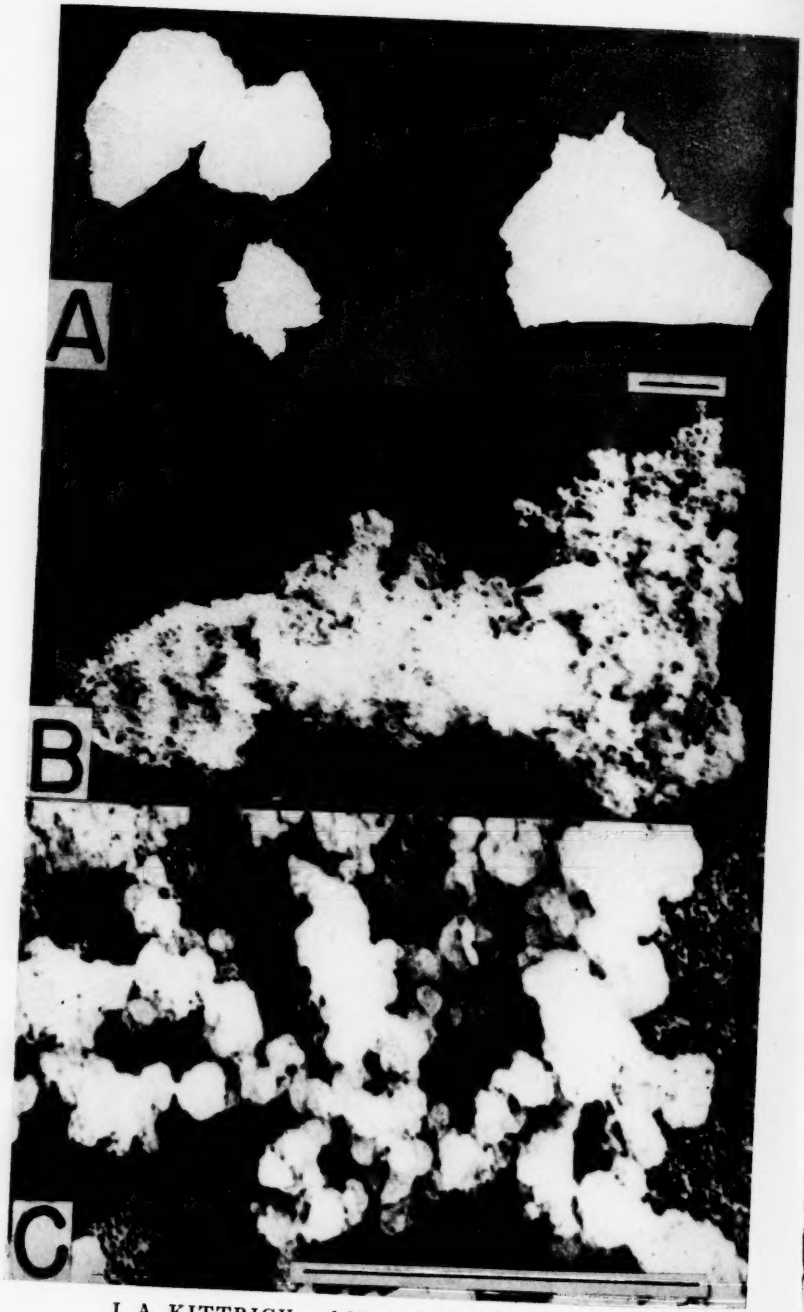
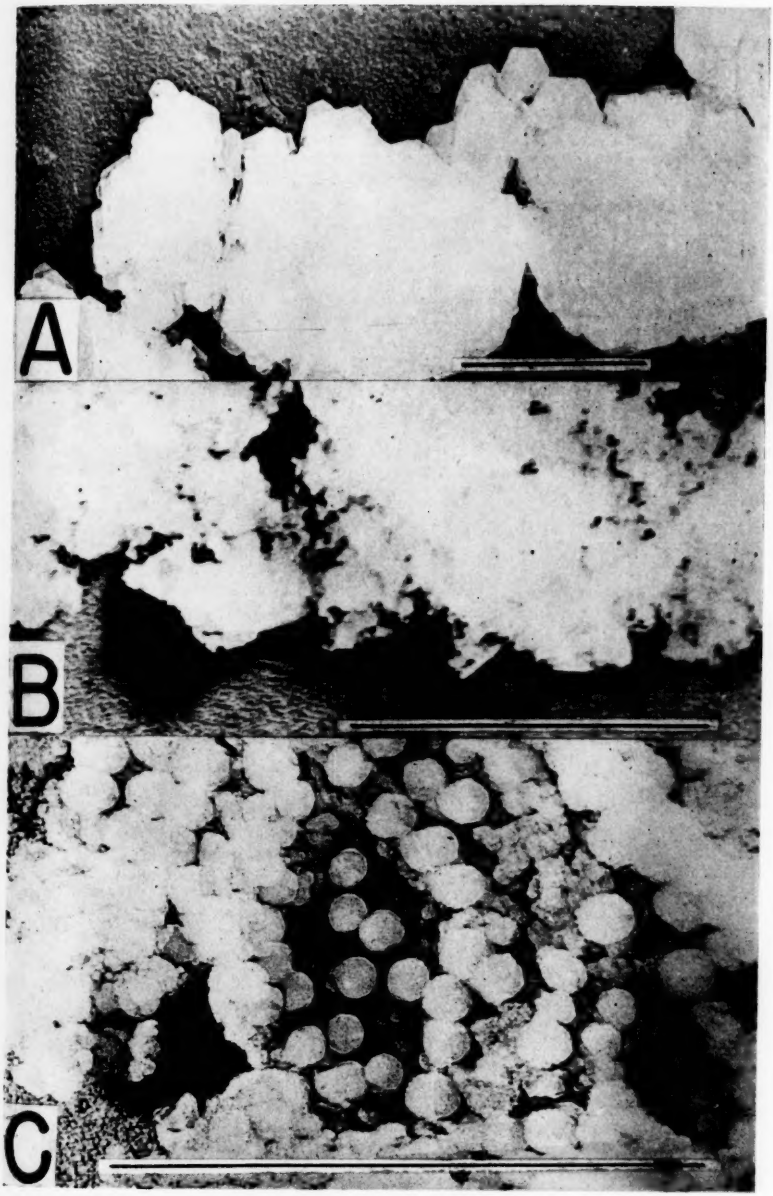


J. A. KITTRICK *and* M. L. JACKSON—PLATE I



J. A. KITTRICK *and* M. L. JACKSON—PLATE II



J. A. KITTRICK *and* M. L. JACKSON—PLATE III

Description of Plates

PLATE I

Electron micrographs of various stages in the phosphate treatment of greenalite at 90° C. Line indicates 1 μ. A. Greenalite particles (2–5 μ). B. New crystal phase resulting from the treatment of greenalite with 1·0 *M* NaH_2PO_4 of pH 4·3 for 11 days. This new crystal phase (product 16) gave a distinct X-ray pattern that could not be identified in the literature. Notice the partially decomposed greenalite crystal present. C. New crystal phase resulting from the treatment for 11 days of greenalite with 1·0 *M* KH_2PO_4 adjusted to pH 7·0 with KOH. This new crystal phase gave an X-ray pattern similar to product 1 (Haseman *et al.*, 1951).

PLATE II

Electron micrographs of the various stages in the phosphate treatment of greenalite at room temperature. Line indicates 1 μ in A and B, but 0·5 μ in C. A. Untreated greenalite (2-5 μ). B. Greenalite treated with 1·0 *M* NaH_2PO_4 of pH 4·3 for 20 months, showing fleecy residue and possible new phosphate phase. C. New phosphate phase resulting from the treatment of greenalite with 1·0 *M* KH_2PO_4 of pH 4·3 for 20 months.

PLATE III

Electron micrographs of the various stages in the phosphate treatment of kaolinite at room temperature. Line indicates 1 μ. A. Untreated kaolinite (−2 mm.). B. Kaolinite treated with 1·0 *M* KH_2PO_4 of pH 4·3 for 23 months showing fleecy residue and possible new rectangular crystal (arrow). The new crystal phase gave an X-ray pattern identical with that of taranakite $K_2Al_2(PO_4)_3 \cdot 7{\cdot}5\,H_2O$. C. New phosphate phase resulting from the treatment of kaolinite with 1·0 *M* NaH_2PO_4 of pH 4·3 for 23 months.

DISTRIBUTION OF PHOSPHORUS IN PROFILES AND PARTICLE-SIZE FRACTIONS OF SOME SCOTTISH SOILS

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THE work reported in this paper forms part of a long-term investigation of the phosphorus relationships of the soil associations in north-east Scotland, designed to integrate the results of complementary field, pot, and laboratory experiments. The categories of phosphorus present, the phosphate-sorption characteristics, and other relevant properties of surface soils from field-experiment areas distributed over the main soil associations are being examined. The present results represent an extension of this scheme to cover seven soil profiles from sites adjoining long-term experiments with lime and phosphate.

There is an extensive literature on the categories of phosphorus in soils, but little information on the phosphorus contents of particle-size fractions. Since the release of phosphorus to both plants and extracting agents depends on particle size as well as chemical form, particular attention has been paid to the content and solubility of phosphorus in the four conventional fractions. An account of the fractionation procedure and of the general distribution of total, total organic, and total inorganic phosphorus is given below, together with data on phosphorus soluble in 0·2 N H_2SO_4, the acid-oxalate reagent of Tamm (1922), and the hydrosulphite-HCl extraction described by Mackenzie (1954). In the treatment of the results attention is concentrated mainly on chemical relationships and the influence of parent material and drainage conditions.

Soils

The seven profiles represent four of the main soil associations in north-east Scotland and include three pairs of corresponding freely drained and poorly drained members as shown in Table 2. They conform with the general characteristics described by Glentworth *et al.* (1947, 1949), and for the present purpose it suffices to mention that the most striking morphological contrasts arise from differences in drainage. The subsoils 4*b*–4*e* and 6*b*–6*d* of the poorly drained basic igneous and granitic profiles show contrasting yellow and grey mottling characteristic of gley soils formed under a seasonally fluctuating water table. Due to the presence of indurated layers, 3*e* and 5*c*, the corresponding freely drained profiles, also show distinct mottling in the lower horizons. All these features are supported by the iron and aluminium values given in Table 2. The poorly drained members have lower oxalate-soluble aluminium throughout the profile and lower hydrosulphite-soluble iron in the

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upper horizons, but in the lower horizons the mottling is reflected in much higher iron values for the gleyed subsoils.

The iron and aluminium values in Table 2 also suggest an influence of parent material, in that comparison of the four freely drained profiles indicates generally higher levels in the basic igneous and slate soils than in the others.

Methods

Separation of particle-size fractions. The necessity for avoiding extensive solution of phosphorus and disturbance of its natural distribution precluded the use of a drastic dispersion treatment. Mechanical dispersion of some of the soils in water, with and without the addition of coarse sand (Puri, 1949), and in a 20 per cent. solution of CCl_4 in methanol (D'Hoore and Fripiat, 1948), was therefore tested. These tests covered different periods and vigour of shaking and showed that simple dispersion in water was highly effective. A dispersion based on shaking 50-g. lots of soil in 500 ml. distilled water on a rapid reciprocating shaker for 16 hours was therefore adopted for carrying out large-scale separations to provide bulk samples of the fractions.

The remainder of the separation was carried out by sedimentation and sieving along the usual lines to give air-dry fractions. The sedimentation was interrupted after the bulk of the clay had been removed in order to sieve off the coarse sand. The clay removal was then completed and followed by separation of the silt and fine sand in the normal way. The clay suspensions were flocculated with a little $CaCl_2$ which, by virtue of the salt effect (Mattson, Williams, Eriksson *et al.*, 1950), also served to minimize losses of phosphate in solution. In the final stages the $CaCl_2$ was removed by dialysis. The clay was then redispersed to give a 0·5 per cent. suspension, recovered by passing through a super-centrifuge using the finest drag, dried at room temperature and ground to pass a 100-mesh sieve. All fractions were then stored in the air-dry condition.

Total phosphorus was determined by the method described by Muir (1952) which is essentially a fusion of soil $<$ 100 mesh with sodium carbonate, followed by colorimetric estimation of phosphate in the water extract of the melt.

Total organic phosphorus was measured as the increase in inorganic phosphorus extracted by 0·2 N H_2SO_4 (2 g. soil $<$ 2 mm., 100 ml. acid, overnight shaking) following ignition of the soil at 550° C. for 1 hour. A full account of this method and of tests carried out to establish the validity of the results is given by Saunders and Williams (1955).

Total inorganic phosphorus was obtained by difference between the total and the total organic phosphorus.

Acid-oxalate and sodium-hydrosulphite extractions for aluminium, iron, and phosphorus (total P extracted) were carried out according to Tamm (1922) and Mackenzie (1954), respectively.

Colorimetric estimations. All iron, aluminium, and phosphorus estimations were done colorimetrically. Except in the total-phosphorus method where hydrazine-sulphate reduction was used, all the phosphorus

estimations were done by the stannous-chloride method as described by Williams and Stewart (1941).

Iron was estimated with dipyrydyl following reduction with hydroxylamine hydrochloride, and aluminium was determined by the aluminon method described by Robertson (1950).

Other determinations were carried out by standard methods.

Results and Discussion

Efficiency of the particle-size fractionation. The recovery of soil was practically complete in all cases and the particle-size composition based on the weights of fractions and total soil recovered is given in Table 1.

TABLE 1

Particle-size Composition based on Large-scale Separations— % on Oven-dry Basis*

Sample† no.	*Coarse sand*	*Fine sand*	*Silt*	*Clay*
1*a*	19	35	25	21
1*b*	20	33	22	26
2*a*	18	39	23	20
2*b*	14	35	25	26
3*a*	27	34	21	18
3*c*	32	35	19	14
3*d*	34	36	15	15
4*a*	30	37	17	16
4*b*	35	39	13	14
4*c*	27	43	14	16
5*a*	50	27	13	10
5*b*	48	29	15	8
5*c*	49	30	14	7
6*a*	55	22	13	11
6*b*	41	35	17	8
6*c*	51	26	11	12
7*a*	19	28	31	22
7*b*	15	50	26	9

* Calculated from weights of fractions and total soil recovered.
† For profile identifications see Table 2.

These values have been compared with results by the International Method by calculating both sets on the basis of weights of the ignited fractions as percentages of the air-dry soils. To save space the detailed results are not included, but they show that the agreement for total sand and total silt plus clay is satisfactory in all cases. For 15 out of the 18 samples the agreement for the individual coarse- and fine-sand values is also satisfactory. With the remaining three samples (3*c*, 4*b*, 4*c*) the large-scale treatment caused extensive breakdown of the coarse sand, amounting to 25 per cent. of the International value for 3*c* and 4*b*, and 50 per cent. for 4*c*. This breakdown is reflected almost entirely as higher values for fine sand. The main disagreement in the comparison, however, is higher silt and lower clay values from the large-scale method.

This indicates incomplete dispersion, and direct analyses of the bulk silt fractions by the International Method show that they contain 6–17 per cent. clay, the contamination being greatest for the topsoils.

The large-scale separations do not therefore conform exactly to those obtained by the International Method, but the agreement in most instances is good and sufficiently close for the bulk fractions to be referred to by the standard names. As is explained below, it can also be accepted that they provide a valid basis for determining the general distribution of phosphorus.

Calculation of F-values. The term 'F-value' is introduced to denote the quantity of phosphorus (total, inorganic, organic, &c.) present in a given particle-size fraction in 100 g. oven-dry soil. Thus the F-values combine the phosphorus contents of the fractions and the particle-size composition of the soil. For example, if the soil contains y per cent. of a particle-size fraction containing f mg. P_2O_5 per 100 g. fraction, then the F-value (per 100 g. soil) $= \frac{yf}{100}$ mg. P_2O_5. For this purpose, the particle-size composition in Table 1, calculated from the actual weights of fractions obtained in the large-scale separations, has been used. Thus, the sum of the F-values for the four fractions is directly comparable with the value determined on the original soil, enabling the validity of the results to be easily checked. The appropriate sums of F-values are included in the tables, but to economize in space the individual F-values, representing the absolute contributions of the fractions to the soil values, are omitted in favour of the relative contributions obtained by expressing each F-value as a percentage of the sum of F-values.

Test calculations have shown that, with the present data, the broad distribution of the different categories of phosphorus is not materially altered by making corrections for discrepancies such as the undispersed clay present in the silt fractions. Apart from this, it will be seen later that the major contrasts are best illustrated by comparing the combined sands with the silt plus clay.

Total, Total Organic and Total Inorganic Phosphorus

Soils, Table 2. The total P is high throughout the profiles. In each case the value is highest in the topsoil. This is true also for the organic P and it is particularly noteworthy that 27–67 per cent. of the total P in the topsoils is present in organic form. Except in the granitic pair, where the value is highest in the lowest horizon, the total inorganic P is also highest in the topsoil. Since the profiles are from agricultural land, there is little doubt that all three categories of P in the topsoils have been enhanced by manuring. It is also likely that there has been appreciable enrichment at the expense of the subsoils by upward translocation through the agency of roots. The latter factor is probably a reason why the total P in the granitic profiles is lowest in the first subsoils. In all the other profiles the general trend is for the total P to decrease downwards and then rise in the lowest horizon. In most instances the main reason for this decrease is a marked fall in the organic P, which has also been reported by other workers (Black and Goring, 1953). In the deeper horizons

TABLE 2

Total P* *Contents, Oxalate-soluble* Al_2O_3, *Hydrosulphite-soluble* Fe_2O_3, *and* pH *Values for Soils*

Sample no.	Depth inches	mg. P_2O_5/100 g. O.D. soil			Org. P as % of total P	% on O.D. soil		pH
		Total	Total org.	Total inorg.		Al_2O_3	Fe_2O_3	
Freely drained profile on Old Red Sandstone till—Laurencekirk Association								
1*a*	0–6	270	130	140	48	0·33	1·93	6·6
1*b*	10–14	220	124	96	56	0·33	1·58	6·3
1*c*	17–21	226	120	106	56	0·29	0·95	6·1
Poorly drained profile on Old Red Sandstone till—Laurencekirk Association								
2*a*	0–6	236	90	146	38	0·22	1·64	7·0
2*b*	9–13	197	95	102	48	0·16	1·48	6·6
2*c*	15–19	145	75	70	52	0·21	0·82	6·3
2*d*	23–27	114	28	86	25	0·23	1·48	6·0
2*e*	37–41	156	24	132	15	0·21	2·26	6·4
Freely drained profile on basic igneous till—Insch Association								
3*a*	0–6	413	189	224	46	0·62	3·40	5·6
3*b*	8–13	340	191	149	56	0·66	3·20	6·0
3*c*	15–17	252	68	184	27	0·78	1·57	6·1
3*d*	18–21	181	48	133	27	1·22	3·74	6·0
3*e*	26–30	141	30	111	21	0·41	3·06	6·5
3*f*	36–44	252	43	209	17	0·20	3·36	5·8
Poorly drained profile on basic igneous till—Insch Association								
4*a*	0–6	352	93	259	27	0·53	2·64	5·4
4*b*	10–14	237	19	218	8	0·37	2·74	6·2
4*c*	18–22	222	8	214	4	0·35	2·05	6·7
4*d*	26–30	147	12	135	8	0·37	5·04	6·2
4*e*	36–42	286	..	..	..	0·38	4·84	6·5
Freely drained profile on granitic till—Countesswells Association								
5*a*	0–8	238	160	78	67	0·43	1·00	5·8
5*b*	10–14	170	93	77	55	0·99	1·10	5·5
5*c*	14–20	189	9	180	5	0·17	0·82	5·5
5*d*	27–30	186	20	166	11	0·10	1·50	5·6
5*e*	41–46	193	10	183	5	0·08	0·96	5·5
Poorly drained profile on granitic till—Countesswells Association								
6*a*	0–8	215	105	110	49	0·27	0·91	5·7
6*b*	11–16	100	10	90	11	0·07	0·64	5·9
6*c*	22–27	130	10	120	8	0·08	0·98	6·2
6*d*	33–39	180	4	176	2	0·06	0·64	6·4
Freely drained profile on slate till—Foudland Association								
7*a*	0–8	464	241	223	52	0·70	2·46	4·8
7*b*	12–18	232	111	121	48	1·47	1·55	5·5
7*c*	24–30	147	52	95	35	0·77	1·65	5·6
7*d*	36–40	155	47	108	30	0·82	1·56	5·5

* All P contents in all tables are expressed on the oven-dry basis.

both the proportion and the amount of organic P become much lower, and the increases in total P in the lowest horizons are due entirely to clear increases in the inorganic P.

Comparisons between the four associations are subject to agricultural influences, but the results for the freely drained profiles suggest a higher

level of all three categories of P in the basic igneous and slate profiles compared with the other two. The clearest contrasts, however, arise from differences in drainage, and in this respect agricultural differences can be largely discounted because the members of each pair have had the same treatment.

In agreement with the results of Glentworth (1947, 1949) the total P is on the whole lower in the poorly drained members (Table 2). The important point shown by the present results is that this difference is due to the much lower organic-P contents of the poorly drained soils. The total inorganic P actually tends to be higher under the poor drainage conditions, with the result that the proportion of organic P is much lower. This contrast is well illustrated by the topsoils, the mean proportion for the three poorly drained soils being 38 per cent. compared with 50 per cent. for the corresponding freely drained soils.

Glentworth and Dion (1949) also noted that the total P content falls more abruptly in poorly drained profiles. This is also true for the basic igneous and granitic pairs in Table 2, and again the dominant factor is the organic P. The fall in organic P from the topsoil to the first subsoils is much greater in the poorly drained members, and it is noteworthy that the phosphorus in the gleyed subsoils is very largely inorganic. In contrast to this the freely drained subsoils contain considerable amounts of organic P of the order of 20–50 mg. P_2O_5 per 100 g., representing 20–30 per cent. of the total P.

Fractions, Tables 3, 4, and 5. The values for the P contents of all four fractions vary very widely, depending on the soil. In most instances the total P (Table 3) is lowest in the coarse sand and highest in the clay. The sands, however, particularly the fine sands, are rich in phosphorus, but it is present largely in inorganic form. The clays and silts on the other hand contain high proportions of organic P (Table 4). In all samples the content of organic P is highest in the clay, and about 50 per cent. or more of the total P in the clay and silt from the topsoils is organic. Even so, the total inorganic P in most instances, including all the topsoils, is also highest in the clay (Table 5). This emphasizes the generally high total-P content of the clays.

The total-P content of the clay (Table 3) decreases down all the profiles, and this is largely true of the silt also. In the silt the dominant factor is the marked fall in organic P (Table 4), but in the clay the inorganic P (Table 5) also shows large decreases. Otherwise, the changes in P contents with depth are either indefinite or related to parent material and drainage conditions.

Comparison of the four freely drained profiles on the basis of the fractions from the topsoils and first subsoils suggests some possible influence of parent material. The total P content (Table 3) is relatively low for the coarse sands in the granitic profile and high for the fine sands in the basic igneous profile. Since the sands contain little organic P (Table 4) these contrasts are essentially differences in the contents of inorganic P (Table 5). Another apparent effect of parent material is the lower P contents of the clays in the Old Red Sandstone profile (Tables 3, 4, and 5), related to the secondary nature of the parent material. Finally,

TABLE 3

Total P *Contents and Proportions of Total Soil* P *in Fractions*

Sample no.	mg. total P_2O_5/100 g. fraction							Sum of F-values†	% of total soil P in fraction‡				
	Coarse sand	Fine sand	Silt	Clay	Combined sands*	Silt + clay	Ratio, silt+clay to sands		Coarse sand	Fine sand	Silt	Clay	Ratio, silt+clay to sands
1*a*	121	114	231	659	116	426	3·7	259	9	15	22	53	3·0
1*b*	86	86	158	500	86	385	4·5	210	8	13	17	62	3·8
2*a*	164	105	191	550	124	358	2·9	225	13	18	20	49	2·2
2*b*	248	79	121	385	127	256	2·0	193	18	15	16	52	2·1
3*a*	146	260	470	983	210	707	3·4	405	10	22	24	44	2·1
3*c*	106	201	288	635	156	436	2·8	249	14	28	22	36	1·4
3*d*	98	152	204	345	126	275	2·2	171	20	32	18	30	0·9
4*a*	117	339	368	765	240	554	2·3	338	10	37	19	34	1·1
4*b*	82	351	220	168	224	193	0·9	219	13	63	13	11	0·3
4*c*	79	327	216	136	231	173	0·8	214	10	66	14	10	0·3
5*a*	40	94	358	1,250	59	746	12·6	217	9	12	22	58	4·0
5*b*	35	114	299	852	64	506	7·9	163	10	20	28	42	2·3
5*c*	58	306	222	390	152	278	1·8	178	16	51	17	15	0·5
6*a*	43	165	320	870	79	572	7·3	198	11	18	21	49	2·3
6*b*	44	172	65	105	103	78	0·8	97	19	62	11	8	0·2
6*c*	80	236	111	58	133	83	0·6	121	33	51	10	6	0·2
7*a*	260	195	313	1,020	221	606	2·7	427	12	13	23	53	3·2
7*b*	140	106	324	810	114	447	3·9	231	9	23	36	32	2·1

* All P contents for combined sands and silt plus clay take account of the particle-size composition of the soil.
† Compare with total soil P, Table 2 (F-value = mg. P_2O_5 in fraction in 100 g. soil).
‡ F-value as % of sum of F-values.

it is noteworthy that the total- and inorganic-P contents of the sands, particularly the fine sand, increase down the freely drained granitic profile, whereas in the other three profiles the values fall considerably (Tables 3 and 5).

TABLE 4

Total Organic-P Contents and Proportions of Total Soil Organic P in Fractions

Sample no.	mg. organic P_2O_5/100 g. fraction				Sum* of F-values	% of total soil organic P in fraction*			
	Coarse sand	Fine sand	Silt	Clay		Coarse sand	Fine sand	Silt	Clay
1a	0	13	124	367	113	0	4	27	68
1b	12	10	80	262	91	2	3	20	75
2a	0	7	101	330	91	0	2	25	73
2b	31	9	54	255	87	5	3	15	77
3a	38	37	262	614	188	5	7	29	59
3c	0	14	72	317	63	0	8	22	70
3d	11	7	51	133	34	6	6	25	63
4a	21	0	145	378	88	7	0	28	65
4b	22	4	37	38	20	..	..	..	..
4c	3	16	20	39	17	..	..	..	..
5a	12	22	232	836	126	5	5	24	67
5b	2	10	150	564	72	1	4	32	63
5c	3	1	17	92	10	..	..	..	..
6a	2	19	209	480	85	1	5	32	62
6b	1	1	7	35	4	..	..	..	..
6c	0	4	7	10	2	..	..	..	..
7a	63	46	167	517	191	6	6	27	60
7b	35	40	159	405	102	5	20	39	36

* Compare with total soil organic P, Table 2, and see footnotes Table 3.

The P contents of the fractions show marked contrasts according to drainage conditions. As for the soils, the total P in the silt and clay (Table 3) is in general lower, and the value for the clays falls more abruptly, in the poorly drained profiles. It is also noteworthy that the gleyed subsoils, 4*b* and 4*c*, 6*b* and 6*c*, of the poorly drained basic igneous and granitic profiles are the only samples in which the clay does not have a higher total P than the other three fractions. Since the clays and silts are rich in organic P (Table 4) these contrasts are partly a reflection of the much lower organic-P contents under the poor drainage conditions, but this is not the only reason. The results in Table 5 show that in most instances the inorganic P in the clay and silt fractions is also lower in the poorly drained soils. In keeping with this, the fine sands from the gleyed subsoils 4*b*, 4*c*, 6*b*, and 6*c* are richer in inorganic P than the corresponding clays. This also applies to the indurated layer 5*c* and it is noteworthy that in the gleyed subsoil 2*b* the inorganic-P content is highest for the coarse sand. This effect of drainage is best illustrated by comparing the P contents of the combined sands with those of the silt plus clay (Tables 3 and 5). For both total and inorganic P, the values for the sands are higher, and those for the silt plus clay are lower, in the

TABLE 5

Total Inorganic-P Contents and Proportions of Total Soil Inorganic P in Fractions

Sample no.	mg. inorg. P_2O_5/100 g. fraction							Sum of F-values*	% of total soil inorg. P in fraction*				
	Coarse sand	Fine sand	Silt	Clay	Combined sands	Silt + clay	Ratio, silt+clay to sands		Coarse sand	Fine sand	Silt	Clay	Ratio, silt+clay to sands
1a	121	101	107	292	108	191	1·8	146	16	24	18	42	1·5
1b	74	76	78	238	75	165	2·2	119	13	21	14	52	1·9
2a	164	98	90	220	119	150	1·3	134	22	29	16	33	1·0
2b	217	70	67	170	112	120	1·1	106	29	24	16	31	0·9
3a	108	223	208	369	172	282	1·6	217	14	35	20	31	1·0
3c	106	187	216	318	148	259	1·8	186	18	36	22	24	0·9
3d	87	145	153	212	117	183	1·6	137	21	39	17	23	0·7
4a	96	339	223	387	230	300	1·3	250	12	50	15	23	0·6
4b	60	347	183	130	211	156	0·7	199	11	67	12	10	0·3
4c	76	311	194	97	220	142	0·6	197	10	68	14	8	0·3
5a	28	72	126	414	43	251	6·0	91	15	21	19	45	1·8
5b	33	104	149	288	59	160	2·7	93	17	34	24	25	1·0
5c	55	305	205	298	150	236	1·6	168	16	54	17	13	0·4
6a	41	146	111	390	71	239	3·4	113	20	28	13	38	1·0
6b	43	172	58	70	102	62	0·6	93	19	65	11	5	0·2
6c	80	232	104	48	131	75	0·6	119	34	51	10	5	0·2
7a	197	149	146	503	170	294	1·7	236	16	18	19	47	2·0
7b	105	66	165	405	75	227	3·0	129	12	26	33	29	1·6

* Compare with total soil inorganic P, Table 2, and see footnotes Table 3.

poorly drained profiles. As a result the ratios of the values silt plus clay to sands are very much lower in the poorly drained members. Thus, under the poor drainage conditions the coarser fractions are absolutely and relatively richer in phosphorus.

Contributions of fractions to soil values (*Tables 3, 4, and 5*). The results in Table 3 show that the sums of F-values for total P are lower than the values determined on the original soils (Table 2). The deficits can be attributed mainly to losses in solution during the separations, but the sum of F-values also combines the errors of four P estimations. Samples *4b*, *5a*, *5c*, *6a*, *6c*, and *7a* show deficits of the order of 6–9 per cent., but the discrepancy for most of the other twelve samples is less than 5 per cent. Considering the prolonged treatments involved, these losses are low, and the fact that they can be attributed mainly to the clays, which are relatively rich in phosphorus, minimizes their importance. The sum of F-values for total inorganic P (Table 5) in most instances agrees very satisfactorily with the value for the original soil (Table 2). But, in keeping with the fact that all the organic-P values are obtained by difference and are subject to greater errors (Saunders and Williams, 1955), the comparison between the sums of F-values for organic P (Table 4) and the values for the original soils (Table 2) is rather variable. On the whole, however, the two sets of values are similar, and the fact that the clays and silts are relatively very rich in organic P makes the discrepancies unimportant. The results provide a valid picture of the general distribution of the three phosphorus categories in the original soils.

The proportion values in Tables 3, 4, and 5 bring out several striking points. The topsoils (Table 3) contain 9–13 per cent. of their total P in the coarse sand and 12–37 per cent. in the fine sand, with totals of 21–47 per cent. present in the combined sands. For inorganic P (Table 5) the corresponding ranges are 12–22, 18–50, and 34–62 per cent. The sand fractions thus account for large proportions of the total and inorganic P in the soils. The organic P (Table 4), on the other hand, is concentrated very largely in the clay and silt. In most instances the clay accounts for 60 per cent. or more of the soil organic P. The contributions of the silt are mostly of the order of 25–30 per cent., and the clay and silt together account for 85 per cent. and more of the soil organic P.

The proportion of the total and inorganic soil P present in the sand fractions shows a general tendency to increase down the profiles (Tables 3 and 5). In some cases this decrease is accentuated by a marked fall in the clay contents (Table 1), but in most cases the actual P contents of the clays and silts decrease down the profiles (Tables 3, 4, and 5).

The main effect of parent material is that the sands, particularly the fine sands, account for higher proportions of the total and inorganic P in the freely drained basic igneous soils (profile 3) than in the others (Tables 3 and 5). The most striking contrasts, however, are again attributable to drainage conditions. Irrespective of parent material, the proportions of the total and inorganic soil P present in the sand fractions are higher in the poorly drained profiles. This contrast is best illustrated by the ratios of the values for the combined sands compared with the silt plus clay, which are much higher for the poorly drained soils (Tables

3 and 5). From Table 1 it can be seen that this greater importance of the sands in the poorly drained soils is not merely an expression of differences in particle-size composition. The dominant factor is that, as already noted, the sands are richer, while the clay and silt are poorer, in phosphorus under the poor drainage conditions. It is particularly noteworthy that in the gleyed subsoils, 4*b*, 4*c*, 6*b*, of the basic igneous and granitic profiles the combined sands account for about 75–85 per cent. of the total and inorganic soil P, compared with 50–60 per cent. for the freely drained subsoils, 3*c*, 3*d*, and 5*b* (Tables 3 and 5).

0·2 N H_2SO_4-*Soluble Inorganic Phosphorus*

Soils, Table 6. This extraction forms part of the organic-P estimation (Saunders and Williams, 1955). The values for the soils cover a wide

TABLE 6

Soil P *Extracted by* 0·2 N H_2SO_4 *Acid-oxalate and Sodium-hydrosulphite—*HCl *methods*

Sample no.*	*0·2 N* H_2SO_4		*Acid-oxalate*		*Hydrosulphite*—HCl	
	Inorg. P_2O_5 *ext. mg./100 g.*	*% of total soil inorg.* P	*Total* P_2O_5 *ext. mg./100 g.*	*% of total soil* P	*Total* P_2O_5 *ext. mg./100 g.*	*% of total soil* P
1*a*	98	70	172	64	81	30
1*b*	52	54	127	58	41	19
1*c*	70	66	147	65	35	16
2*a*	97	67	140	59	87	37
2*b*	44	43	115	58	39	20
2*c*	28	38	67	46	35	24
2*d*	38	44	50	44	41	36
2*e*	88	67	74	48	71	46
3*a*	139	64	224	55	53	13
3*b*	98	66	182	54	31	9
3*c*	117	64	116	46	38	15
3*d*	74	55	66	36	42	23
3*e*	43	39	40	28	50	35
3*f*	144	69	79	31	84	33
4*a*	243	94	157	45	84	24
4*b*	197	90	48	21	48	21
4*c*	188	88	46	21	56	25
4*d*	123	91	35	24	40	27
4*e*	..	..	50	18	41	14
5*a*	78	100	155	65	57	24
5*b*	60	78	164	97	27	16
5*c*	169	94	68	36	89	47
5*d*	150	90	66	36	95	51
5*e*	165	90	60	31	120	62
6*a*	90	82	121	56	63	29
6*b*	85	94	17	17	58	58
6*c*	110	92	21	16	55	42
6*d*	165	93	22	12	75	42
7*a*	150	67	344	74	122	26
7*b*	66	55	138	59	46	20
7*c*	50	53	69	47	48	33
7*d*	46	43	70	45	46	30

* For profile identifications see Table 2.

range (Table 6). The proportion of the total inorganic P extracted ranges from 38 to 100 per cent., and tends to follow the absolute values. Like the total inorganic P (Table 2) the H_2SO_4 values for the basic

igneous and granitic profiles tend to be higher in the poorly drained members. Similarly, both the total inorganic and the H_2SO_4-soluble P increase down the granitic profiles (Nos. 5 and 6) whereas the other profiles show the reverse tendency. Otherwise, the values for the soils show no striking features.

Fractions, Table 7. Several features of the results emphasize the importance of the sand fractions in the H_2SO_4 extractions. In half of the samples, including all the basic igneous soils (profiles 3 and 4), the absolute value is highest in the fine sand; for samples *2a* and *2b* it is highest in the coarse sand, and in only 7 out of the 18 soils is it highest in the clay. The most striking feature, however, is that in practically all the samples the proportion of the total inorganic P extracted is highest for the fine sand; further the degree of extraction in virtually all cases is over 70 per cent. and in several cases practically complete. The proportions extracted from the coarse sands are also high, the value in most cases being in the range 50–100 per cent. The percentage extraction of the silts is also over 50 in most cases, but for 11 out of the 18 samples the value for the clay is less than 50 per cent. and in only three cases does it exceed 60 per cent.

The results in Table 7 show that the drainage contrast is again illustrated by higher values for the combined sands and lower values for the silt plus clay in the poorly drained profiles. In the basic igneous and granitic profiles (Nos. 3 and 4, 5 and 6), not only are the sands in the poorly drained members (Nos. 4 and 6) richer in inorganic phosphorus, but the phosphorus is also more soluble, as shown by the higher degree of extraction. Similarly, in both the granitic profiles the degree of extraction as well as the absolute value increase with depth.

Contributions of fractions to H_2SO_4 *soil values, Table 7.* Since 0·2 N H_2SO_4 is a strong extracting agent and the extraction conditions can be varied considerably with little effect on the results, it is justifiable to calculate F-values on the basis of the standard extractions of the fractions. In agreement with this the sums of the F-values (Table 7) are in most instances very similar to the H_2SO_4 values for the original soils (Table 6). The distribution values are therefore valid, and they show even more clearly the importance of the sand fractions, especially in the poorly drained soils. In general, 30–95 per cent. of the H_2SO_4-soluble inorganic P is derived from the sands.

Acid-Oxalate- and Acid-Hydrosulphite-Soluble Phosphorus, Table 6. The results for these two extractants represent the total P in the extracts. The values in both cases cover wide ranges, and the proportions of the total soil P extracted vary from 12 to 97 per cent. for the oxalate, and from 9 to 62 per cent. for the hydrosulphite.

Several features of the oxalate results indicate that the values are considerably influenced by organic phosphorus. The amount extracted is high in the topsoils and those subsoils, such as *1b*, *1c*, *3b*, *5b*, and *7b*, where the organic phosphorus is high (Table 2). For most of these samples the oxalate values are higher than the total inorganic phosphorus, (Table 2) and, of course, higher than the H_2SO_4 and hydrosulphite values. The oxalate values also show the same general trends

TABLE 7

0·2 N H_2SO_4-*soluble Inorganic*-P *Values for Fractions*

Sample no.	*mg. inorg.* P_2O_5/100 *g. fraction*				*% ext. of total inorg. P in fractions*				*Sum of F-values**	*% contribution of fractions to soil values**				
	Coarse sand	*Fine sand*	*Silt*	*Clay*	*Coarse sand*	*Fine sand*	*Silt*	*Clay*		*Coarse sand*	*Fine sand*	*Silt*	*Clay*	*Ratio, silt+clay to sands*
1*a*	72	79	71	167	60	78	66	57	95	15	30	19	37	1·2
1*b*	45	59	46	185	61	78	58	78	86	10	22	12	56	2·1
2*a*	87	71	66	76	53	73	73	35	74	22	38	20	20	0·7
2*b*	87	49	31	50	40	70	46	29	50	24	34	16	26	0·7
3*a*	77	195	108	127	72	87	52	35	135	16	50	17	17	0·5
3*c*	57	155	91	113	54	83	42	35	105	17	51	16	15	0·5
3*d*	44	107	59	73	51	74	39	34	75	20	53	12	15	0·4
4*a*	88	339	153	189	92	100	69	49	205	13	61	13	14	0·4
4*b*	71	347	147	46	100	100	80	35	186	13	73	10	4	0·2
4*c*	60	311	155	44	79	100	80	45	179	9	75	12	4	0·2
5*a*	18	60	87	244	64	83	69	59	60	15	27	18	40	1·4
5*b*	24	84	70	114	73	81	47	61	56	21	43	20	16	0·6
5*c*	43	295	184	200	78	97	90	67	150	15	59	17	9	0·4
6*a*	27	136	77	202	66	93	69	52	77	19	39	13	29	0·7
6*b*	33	169	34	18	77	98	59	26	80	17	74	8	1	0·1
6*c*	73	236	32	13	91	100	31	27	103	35	59	4	2	0·1
7*a*	81	105	82	298	41	70	56	59	135	11	22	18	49	2·0
7*b*	21	34	87	175	20	52	53	43	59	5	29	39	27	1·9

* Compare with soil values, Table 6, and see footnotes Table 3.

with depth and drainage as the organic-phosphorus values (Table 2) whereas the hydro-sulphite values do not.

Where the organic phosphorus is very low, as in several of the lower subsoils, the hydrosulphite values are similar to or higher than the oxalate values. In particular, the hydrosulphite values are clearly higher than the oxalate for the granitic subsoils 5*c*–5*e* and 6*b*–6*d*. This could be due to some extent to greater extraction of Fe- and Al-bound P from the silt and clay, but greater extraction of acid-soluble P from the sands is almost certainly the main factor. For samples 5*c*, 6*b*, and 6*c*, the detailed results (which are not included) for the fractions show that the hydro-sulphite-soluble P is greater than the combined contribution of the silt plus clay to the total inorganic soil P. Further, the differences between the hydrosulphite and oxalate values are greater than the total organic-P contents of the soils (Table 2). For these three samples, therefore, the hydrosulphite method extracts inorganic phosphorus from the sands, which account for 70–85 per cent. of the total soil inorganic P (Table 5). There is little doubt, therefore, that the hydrosulphite extraction is generally more effective than the oxalate in dissolving phosphorus from the sands. The difference becomes evident as higher hydrosulphite values only where the organic P is low and the proportion of the soil inorganic P in the sands is high. In agreement with this the hydro-sulphite-soluble P also tends to be higher than the oxalate values for samples 3*e*, 3*f*, 4*c*, and 4*d*, all of which are from the basic igneous profiles which are characterized by high proportions of inorganic phosphorus in the sands (Table 5).

General Discussion

The results for the whole soils show several clear trends, particularly for organic P, but the values for the fractions are more instructive and reveal several differences which would not otherwise be apparent. The main features and implications of the results are as follows:

Organic P. The organic P is concentrated largely in the clay and silt and accounts for 27–67 per cent. of the total P in the topsoils. The poorly drained soils have much lower organic-P contents. There are probably two main factors involved. Poorer drainage can be expected to result in poorer growth and lower returns of organic P as plant residues. In particular, poorer root development and penetration are probably important, especially in relation to the abrupt fall in organic P from the topsoil to the first subsoil in the poorly drained profiles. The fact that the contrasts and changes are much less marked in the Old Red Sandstone pair (Table 2) can be attributed to the nature of the parent material and to longer and more intensive cultivation and manuring, all conducive to freer drainage and deeper root penetration. In addition to lower returns, there are probably greater losses of organic P from the poorly drained profiles. Their generally higher pH and lower sesquioxide content (Table 2) are less favourable for the retention and stabilization of organic phosphates (Black and Goring, 1953). Anderson (1955) has recently shown that some of the soils contain phytic-acid derivatives, which are stabilized in combination with iron and

aluminium in acid soils. In the upper horizons where the bulk of the organic P occurs, the freely drained profiles are richer in both these constituents. At the pH prevailing, the important factor may be the formation of aluminium rather than ferric phytate, and it is probably significant that the oxalate-soluble aluminium is higher throughout the freely drained profiles (Table 2). The fact that, despite their high iron contents, several gleyed subsoils, particularly 4*d* and 4*e* (Table 2), contain practically no organic P is also compatible with the suggestion that aluminium is the more important factor. Another relevant point is that the acid-oxalate extraction strongly reflects the organic P whereas the hydrosulphite method does not (Table 6). The superiority of the oxalate method can be attributed to extraction of both aluminium and ferric phytates by virtue of the strong complexing action of the oxalate ions (Mattson, Williams, and Barkoff, 1950). In the hydrosulphite method there is no strong complexing ion, and the hot-HCl treatment involved extracts very little organic P (Saunders and Williams, 1955).

The fact that the sands also contain significant amounts of soil organic P is of interest in relation to methods of estimation. The organic P in the sands probably occurs to some extent as films coating the mineral particles, but visual examination shows that there are also coarse particles of organic matter present. The organic P in these particles may not be fully accounted for by alkaline-extraction methods, and NaOH extraction tends to give somewhat lower values compared with the ignition—0·2 N H_2SO_4-extraction method (Saunders and Williams, 1955).

Total inorganic P. The outstanding feature of the results is that the sands, particularly the fine sands, have very substantial contents of inorganic phosphorus (Table 5). Since apatites are the principal forms of phosphorus in rocks and have been shown to occur in the coarser fractions of these soils (Hart, 1929, 1941), there is little doubt that the phosphorus in the sands is largely calcium-bound. This is supported by the high solubility of the fine-sand phosphorus in 0·2 N H_2SO_4 (Table 7). In these acid soils the secondary phosphorus of the clays, on the other hand, is undoubtedly iron- and aluminium-bound; its solubility in 0·2 N H_2SO_4, despite the smaller particle size, is much lower than that of the fine-sand phosphorus. Since the silt fractions contain appreciable amounts of clay they also contain sesquioxide-bound phosphorus; but, since apatite is present (Hart, 1929, 1941), they probably contain substantial amounts of calcium-bound phosphorus as well, as indicated by the generally higher H_2SO_4 solubility of the silt phosphorus compared with the clay phosphorus (Table 7). The particle-size fractions therefore differ markedly in the nature as well as in the amounts of inorganic phosphorus present.

The phosphorus in the sands is highly soluble in 0·2 N H_2SO_4 and constitutes a large reserve of potentially available phosphorus. Because of the relatively large particle size, the short-term contribution of the sand, particularly the coarse sand phosphorus, to the nutrition of crops is probably very small, but the substantial amounts of phosphorus in the silts may be of considerable importance. The presence of large and

varying amounts of calcium-bound phosphorus in the sand fractions complicates the problem of evaluating the phosphorus status of the soils, particularly if dilute acid reagents are used.

The inorganic-P values for the fractions (Table 5) emphasize the importance of drainage conditions in the phosphorus relationships of soils. The poorly drained soils have considerably higher amounts and proportions of total inorganic P in the sands and, hence, much lower amounts and proportions in the silt and clay. It appears, therefore, that the poorly drained soils contain more calcium-bound, but less sesquioxide-bound, phosphorus. The dominant factor is that the sand fractions are richer in inorganic P in the poorly drained soils. The inorganic-P contents of the clays, on the other hand, are higher in the freely drained soils. The culmination of this contrast is shown by the gleyed subsoils of the basic igneous and granitic profiles where the sands not only account for 70–85 per cent. of the total soil inorganic P, but the fine sands are actually richer in phosphorus than the clays (Table 5). The fact that the lower inorganic-P contents of the clays in the poorly drained soils are counterbalanced by higher values for the sands and that the total soil inorganic P also tends to be higher in the poorly drained soils militates against extensive mobilization and loss of inorganic phosphorus as such. The lower total-P contents of the poorly drained soils hinge on their lower contents of organic P, and it seems more likely that any losses that occur involve organic rather than inorganic P.

Extraction values. The results for the 0·2 N H_2SO_4, oxalate, and hydrosulphite methods illustrate the usefulness of information on the P contents of the particle-size fractions. Without this guidance the values for the soils are of limited significance. The oxalate and hydrosulphite values have already been discussed; their significance can vary greatly depending on the organic-P content of the soil and the distribution of inorganic P over the fractions.

The dominant factor in the H_2SO_4 extraction is the high degree of extraction of phosphorus from the sands, particularly the fine sand (Table 7). The soil values and the proportions of the total soil inorganic P extracted (Table 6) are in general high where the sands, particularly the fine sands, account for high proportions of the total inorganic P (Table 5). This explains the generally high level of the H_2SO_4 values throughout both the basic igneous profiles and the very high values for the gleyed subsoils of the basic igneous and granitic poorly drained profiles. This association between poor drainage, high sand phosphorus, and high H_2SO_4 values is also strikingly demonstrated by the lower subsoils of the granitic freely drained profile, that are gleyed due to the presence of the indurated horizon, 5*c*.

The relative contribution of the fractions to the H_2SO_4 values varies greatly for the different soils. Since the phosphorus appears to be largely calcium-bound in the sands and iron- and aluminium-bound in the clay, it is clear that the chemical significance of the H_2SO_4 values also varies widely. It is noteworthy that this is true for the topsoils, because 0·2 N H_2SO_4 is used for evaluating the phosphorus status of soils (Williams, 1952). For example, the basic igneous and slate freely

drained topsoils, 3*a* and 7*a*, give much the same H_2SO_4 value (Table 6), but the composition of the values differs greatly. In the basic igneous soil 66 per cent. of the H_2SO_4-soluble P is derived from the sands and only 17 per cent. from the clay, whereas in the slate soil there is 49 per cent. from the clay and only 33 per cent. from the sands. The 0·2 N H_2SO_4 reagent is known to give useful evaluations of phosphorus status for many soils and the main objective in using it is to obtain an integrated measure of the supply of available phosphorus. Differences in the composition of the H_2SO_4 values, therefore, do not necessarily mean that their significance as criteria of phosphorus status also differs. That must be decided in the light of correlations with the responses of crops to phosphate. However, where such correlations are poor or vary according to parent material and drainage conditions, differences of the above kind provide an explanation. The correlations for the present soil associations have not yet been tested, but the generally high level of the values, the high degree of extraction and strong influence of the sands, and the marked variations in the composition of the values would appear to be unfavourable factors.

Parent material and drainage. Several influences of parent material on the phosphorus relationships of the soils have been noted, particularly the higher inorganic-P values for the sands in the basic igneous soils and the lower P contents of the clays in the Old Red Sandstone soils (Table 5). The basic igneous and slate soils also have rather higher P, Fe, and Al contents (Table 2). The outstanding feature of the results, however, is that the major contrasts hinge on drainage conditions. The numerous effects of this factor are noted in the summary, and in conclusion it can be said that the results for the fractions clarify the significance and emphasize the importance of drainage conditions in the phosphorus relationships of the soils.

Summary

1. The distribution of total, total organic, total inorganic, and 0·2 N H_2SO_4-soluble inorganic P has been determined for soil samples and particle-size fractions representing horizons from seven profiles, covering four main soil associations in north-east Scotland and including three pairs of corresponding freely drained and poorly drained members. For the soils, aluminium, iron, and total P extracted by Tamm's acid-oxalate method and Mackenzie's hydrosulphite method have also been determined.

2. Simple dispersion in water enabled representative bulk samples of the particle-size fractions to be separated with little loss of phosphorus and minimum disturbance of its natural distribution.

3. The total soil P decreases down all the profiles, reflecting mainly a marked fall in the organic P.

4. The clay and silt together contain 85 per cent. and more of the total soil organic P, but the sands also contain appreciable amounts, present in coarse particles of organic matter, and it is unlikely that this phosphorus is completely extracted by alkaline reagents. In the topsoils

the proportions of the total P in organic form are 27–67 per cent. for the soils and 50–65 per cent. for the clays and silts.

5. The P contents of the fractions vary widely depending on the soil, but the total P is normally highest in the clay and lowest in the coarse sand, the main exceptions being the gleyed subsoils where the fine sands are richer than the clays.

6. The phosphorus in the sands is largely inorganic and in about half of the samples, including most of basic igneous soils and the gleyed subsoils, the fine sand is richer in inorganic P than the clay.

7. In the topsoils the coarse sands account for 12–22 per cent. of the total soil inorganic P and the fine sands for 18–50 per cent., giving totals of 34–62 per cent. in the combined sands. The tendency is for these proportions to increase with depth, and in the gleyed subsoils the values for the combined sands are of the order of 70–80 per cent.

8. The inorganic P in the sands, particularly the fine sand, is very highly soluble in 0·2 N H_2SO_4 and appears to be largely calcium-bound. For most of the samples, 50–80 per cent. of the inorganic P extracted by this reagent is derived from the sands, but the composition and significance of the values vary widely depending on the distribution of phosphorus over the fractions. This is true also for total P by the oxalate and hydrosulphite methods. The latter, particularly, attacks the sands to varying extents, and the oxalate values are strongly influenced by organic P.

9. The main effect of parent material is that the sands, particularly the fine sands, are richer in phosphorus and account for higher proportions of the total soil P in the basic igneous soils. These soils are also relatively rich in aluminium and iron.

10. The results emphasize the importance of drainage conditions in the phosphorus relationships of the soils. In general, poor drainage is reflected in: (*a*) much lower total organic P, lower total P, but rather higher total inorganic P; (*b*) a very abrupt fall in the organic P with depth; (*c*) higher P contents for the sands, but much lower contents in the clays; (*d*) higher amounts and proportions of the soil inorganic P present as sand and correspondingly lower amounts and proportions as clay; (*e*) higher acid-soluble inorganic P in the soils, reflecting both the higher amounts and higher solubility of the phosphorus in the sands; and (*f*) lower contents of hydrosulphite-extractable iron in the upper horizons but higher contents in the gleyed subsoils, and lower oxalate-soluble aluminium throughout the profiles.

11. The implications of the results are discussed with particular reference to the variations in organic P and the significance of the large and varying amounts of acid-soluble P in the sands in relation to phosphorus status.

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DIAGNOSTIC TECHNIQUES FOR THE SALINE AND ALKALI SOILS OF THE INDIAN GANGETIC ALLUVIUM IN UTTAR PRADESH

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In a previous paper Agarwal and Yadav (1954) presented some data on the appraisal of soil salinity in the saline and alkali soils of the Indian Gangetic alluvium on the lines recently developed by the U.S. Salinity Laboratory (Handbook, 1954). The experimental results given in the paper showed very high pH values for those soils and an almost complete absence of gypsum in both soils and sub-soils. Furthermore, the composition of the saturation extracts from the surface soils showed that the contents of sodium ions were unusually high. The presence in some cases of a semi-indurated bed of calcium-carbonate nodules or clay pan in the sub-soils that obstructed drainage was an additional distinguishing factor. It was in these important characters that the soils reported in that paper differed essentially from apparently similar soils found in America. In connexion with the developmental project of the Government of Uttar Pradesh for a large-scale reclamation of such land, considerable numbers of samples were referred to this laboratory during the soil survey of the affected areas with a view to their analysis to appraise salinity status and determine the best methods of reclamation. The problem being urgent and of economic importance, it was considered advisable to use techniques for the chemical and physical determinations on those soil samples which could give, rapidly and with reasonable accuracy, a correct idea of the probable response to reclaiming treatments and other management practices. Accordingly, a need arose to study whether the tests and methods proposed for such an appraisal by the U.S. Salinity Laboratory (Handbook, 1954) could be adopted with advantage in the characterization of the saline and alkali soils found in the Indian Gangetic alluvium. The present paper embodies the results and findings of such an investigation in so far as it relates to chemical measurements.

The Handbook (1954) lays down chemical determinations that give precise information on the properties of saline and alkali soils in any problem area. The suggested procedure consists *inter alia* of determining the saturation percentage and the pH values of the soil suspensions. The electrical conductivity of the saturation extracts of the soils is then measured which gives an estimate of the total cationic (or anionic) contents. Further, if the ratio between the bivalent cations and sodium in the saturation extract is known, the exchangeable-sodium percentage in the soil can be calculated. This calculation is based on the validity of the relationship existing between the soluble and exchangeable cations in the soil at its saturation moisture percentage. The above information,

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together with data for quick tests on gypsum, lime, and organic matter, is considered enough to a precise statement about the salinity and alkali status of the soil. However, it is obviously necessary that the applicability of the proposed technique should be fully tested before using it for any other group of soils, especially those developed under different climatic or environmental conditions. If the technique could be applied to the Indian soils, the appraisal would certainly be easy and rapid under both field and laboratory conditions and would greatly assist a scientific programme of large-scale reclamation of such areas.

Material and Methods

In the course of a general soil survey of the saline and alkali areas of the Gangetic alluvium in the central and western parts of Uttar Pradesh, more than two thousand samples of soil were analysed in these laboratories. From the above samples, a fairly representative assortment of soils was made typifying the ranges of salinity and alkali that can be encountered in the natural state in this tract. A further careful selection of samples reduced the number to eighteen, in which the saturation percentage varied from 33 to 100. These selected samples which were all of surface soils had a range of electrical conductivity from about 1 to 60 millimhos per cm. and of pH values from 7·5 to 10·9. Eight samples showed different degrees of calcareousness and the remaining ten were free from insoluble alkaline-earth carbonates.

Methods recommended in the Handbook (1954) were followed for all determinations. Saturation extracts were prepared by following method 3 A, using a tyre pump on a modified Houston Filter apparatus. Determination of the pH values was made by means of a glass electrode and a Macbeth pH meter. Electrical conductivity was measured on a Philips conductivity apparatus. The usual macro-methods were adopted for determining the cationic composition of the saturation and ammonium-acetate extracts, sodium being estimated by the uranyl-zinc-acetate method. Any other special method followed in these studies is mentioned under experimental results.

Experimental Results and Discussions

(i) *Electrical conductivity and cationic concentration.* The measurement of electrical conductivity (E.C.) of the soil solutions is recognized as giving a fair indication of total soil salinity. The special advantage of the measurement of E.C. of the saturation extract of saline soils lies in the fact that it gives rapidly a fair and workable method of appraising soil salinity in relation to plant growth. However, it is now well established that E.C. has very little correlation with the total soluble-salt content of the soil, due to the disturbing influence that the anions have on the values for E.C. in aqueous solutions, although a high degree of correlation exists between this value and the total soluble cations (T.S.C.) of the extracts (Handbook, 1954). Campbell, Bower, and Richards (1948), in their studies of E.C. and ion concentration of saline soils from the western U.S.A., found that a very close correlation exists between the

E.C. and the T.S.C. of the saturation extracts. The equation suggested by them for this correlation is as follows:

$$\text{T.S.C. in m.e. per litre} = 10{\cdot}37 \times (\text{E.C.} \times 10^3)^{1{\cdot}065}$$

Similarly, Fireman and Reeve (1948), describing the characteristics of the saline and alkali soils in Gem County in Idaho (U.S.A.), report excellent relationship between the T.S.C. as determined by chemical analysis and the E.C. of the saturation extracts.

Since data showing the relationship between the E.C. and T.S.C. for saline and alkali soils of the area were not available, an attempt has been made to see whether the relations obtained for the American soils also hold for the Indian soils. Table 1 contains the data on E.C. in millimhos per cm. and cationic concentration in m.e. per litre of the saturation extracts. The T.S.C. in the extracts have been compared with the figures obtained by calculating them according to the equation proposed by Campbell, Bower, and Richards. The ratio between the T.S.C. and E.C. has also been calculated.

It may be observed from Table 1 that the soils selected had a fairly wide range of saturation percentage, varying from 33 to 100 per cent. and a similar wide range of E.C. varying from 0·930 to 60·569 millimhos per cm. Under these conditions, with the exception of one soil (C5770) which had an abnormally high content of sodium, the ratio between the E.C. and T.S.C. varies from 9·89 to 12·31, giving an average figure of 11·13. This signifies a good and workable correlation between the two estimates. These figures are plotted on a graph (Fig. 1) wherein it may be seen that a straight-line correlation has been obtained between the two values giving a correlation coefficient of 0·976, which is significant at 0·1 per cent. level. This high level of correlation obtained for Gangetic alluvial soils is of great significance as it helps considerably in devising suitable diagnostic field and laboratory techniques to appraise salinity for saline areas. The values for T.S.C. in m.e. per litre calculated by the equation proposed by Campbell, Bower, and Richards and those actually determined also show a fair degree of resemblance, especially in the lower salinity range, since in soils of high conductivity the deviation is greater than in those having low or medium salt contents.

(ii) *Cation-exchange capacity and exchangeable cations.* The determinations of the cation-exchange capacity (C.E.C.) and the individual exchangeable cations are of great importance in characterizing saline and alkali soils and in devising suitable reclaiming techniques. Bower, Reitemeier, and Fireman (1952) state that the exchange-cation analysis of the saline and alkali soils is subject to difficulties not ordinarily encountered with normal soils owing to the presence in the former of soluble salts and free carbonates of calcium and magnesium. These workers have shown that neutral ammonium-acetate solution usually employed for the determination of C.E.C. of the soils cannot be so used for some saline and alkali soils as the latter fix appreciable amounts of ammonium ions under moist conditions, thus giving lower values for the C.E.C. They have suggested the use of normal sodium-acetate solution having a pH value of 8·2 for the estimation of C.E.C. To see whether

TABLE I

Electrical Conductivity and Cationic Concentration in Saturation Extracts

Laboratory numbers	*Saturation percentage*	*E.C.* $\times 10^3$	*Cations in saturation extract m.e./litre*				*Total soluble cations m.e./litre*		$\frac{T.S.C.}{E.C. \times 10^3}$
			Ca	Mg	K	Na	*As determined*	*Calculated from the equation* $10{\cdot}37 \times (E.C. \times 10^3)^{1{\cdot}065}$	
C4924	50·0	34·2	15·0	23·5	4·5	295·8	338·8	446·8	9·9
S/C2361	33·4	4·6	4·0	4·5	6·0	32·8	47·3	53·0	10·2
C5770	39·9	60·6	7·0	9·0	7·5	976·6	1,000·1	820·0	16·5
C4959	38·0	21·3	10·0	8·0	4·5	192·0	214·5	269·5	10·1
C6216	49·4	5·2	5·0	1·5	3·0	43·4	52·9	61·4	10·1
S/C2378	44·7	41·4	5·0	7·0	3·8	494·5	510·3	547·4	12·3
C4967	35·9	6·8	10·0	6·0	6·0	48·3	70·3	80·6	10·3
S/C2692	48·0	2·0	1·5	0·5	0·4	19·1	21·5	21·3	10·9
S/C2383	37·9	1·5	2·5	1·0	0·7	12·8	17·0	15·8	11·5
S/C2405	42·9	1·5	1·5	1·5	0·4	13·3	16·7	15·5	11·5
C5333	100·0	3·9	5·0	0·5	0·7	35·0	41·3	44·6	10·5
C5343	93·0	2·0	4·5	1·0	1·1	16·0	22·6	21·3	11·5
C5355	97·1	3·3	3·0	0·7	0·7	31·9	36·4	36·8	11·1
C5354	79·1	4·3	2·0	0·5	0·7	40·2	43·4	48·5	10·2
C5348	51·4	4·8	2·0	1·0	0·4	45·9	49·3	54·8	10·3
C5835	45·4	1·4	1·0	0·2	nil	13·5	14·7	14·6	10·7
C5889	42·0	0·9	2·5	1·5	0·7	5·6	10·4	9·6	11·1
C6203	39·1	1·1	4·0	1·0	1·5	6·7	13·2	11·8	11·8

CONCENTRATION —— MEQ. /L.

these observations were applicable to the saline and alkali soils of Gangetic alluvium, detailed cation-exchange estimations were made, using the methods recommended in the Handbook (1954). The soil was extracted with an excess of normal ammonium-acetate solution and the

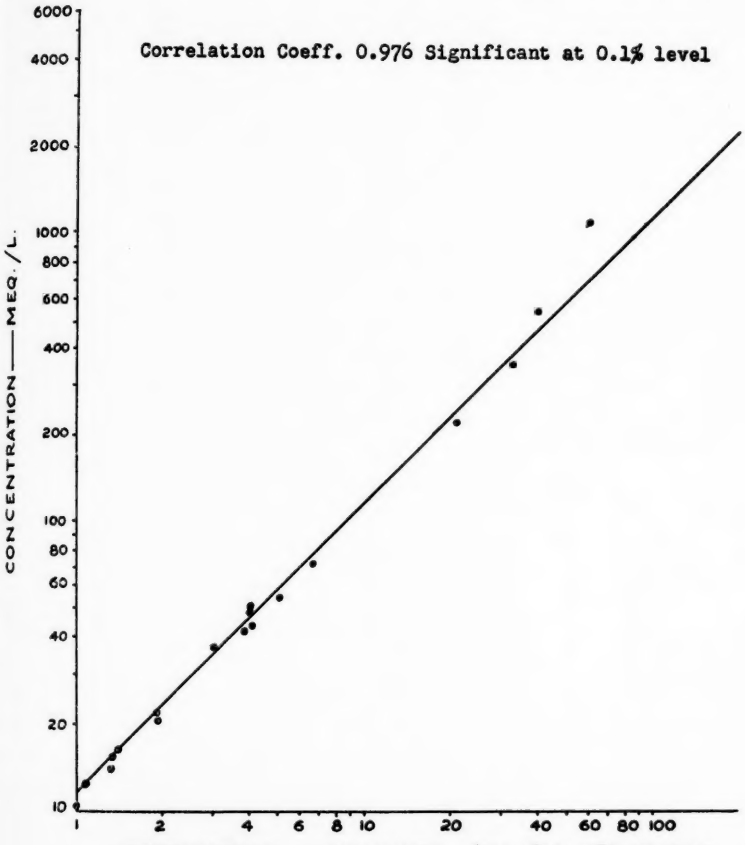

Figure 1. Conductivity and salt concentration in m.eq./litre

milli-equivalents of the various cations removed were estimated. From these figures the amounts of the cations present in the saturation extracts, *vide* Table 1, were subtracted which gave the figures for the individual exchangeable cations in the soils. The total C.E.C. of the soils was determined with ammonium acetate and sodium acetate and also by the summation of the individual cations for the sake of comparison. The data so obtained are presented in Table 2.

An examination of Table 2 reveals that the values obtained for C.E.C. by the ammonium-acetate method are, in every case except soil no.

TABLE 2

Cation Exchange Capacity and Exchangeable Cations in the Saline and Alkali Soils

Laboratory number	*Calcariousness*	*Cation exchange capacity m.e. %*		*NH_4 fixed in non-exchangeable form m.e. %*	*Cations in amm. acetate extract m.e. %*				*Cations in saturation extract m.e. %*				*Exchangeable cations m.e. %*				
		By CH_3COONH_4	*By* CH_3COONa		Ca	Mg	K	Na	Ca	Mg	K	Na	Ca	Mg	K	Na	*Total*
C4924	+ ++	7·9	10·0	+2·1	27·6	2·4	0·6	20·2	0·7	1·2	0·2	14·8	26·8	1·2	0·4	5·4	33·9
S/C2361	+ o	11·3	12·7	+1·4	6·4	0·8	1·2	5·5	0·1	0·1	0·2	1·1	6·3	0·6	1·0	4·4	12·3
C5770	++ ++	8·4	8·6	+0·2	27·6	2·4	0·3	47·0	0·3	0·4	0·3	39·0	27·3	2·0	0·0	8·0	37·4
C4959	++ ++	11·0	11·4	+0·3	38·0	2·4	0·3	12·8	0·4	0·3	0·2	7·3	37·6	2·1	0·1	5·5	45·4
C6216	+	10·2	11·7	+1·5	17·6	1·6	1·8	7·1	0·2	0·1	0·1	2·1	17·3	1·5	1·7	4·9	25·5
S/C2378	++ +	12·9	16·4	+3·6	10·4	0·8	1·5	29·0	0·2	0·3	0·2	22·1	10·2	0·5	1·3	6·8	18·8
C4967	+ ++ +	12·4	13·7	+1·3	35·6	1·6	0·9	6·6	0·4	0·2	0·2	1·7	35·2	1·4	0·7	4·9	42·2
S/C2692	o	10·6	12·0	+1·4	8·0	0·4	0·6	4·2	0·1	0·0	0·0	0·9	7·9	0·4	0·6	3·2	12·1
S/C2383	o	10·1	13·5	+3·5	7·2	0·8	1·2	2·7	0·1	0·0	0·0	0·5	7·1	0·8	1·2	2·2	11·3
S/C2405	+ ++	8·7	11·3	+2·6	63·2	1·6	1·2	5·3	0·1	0·1	0·0	0·6	63·1	1·5	1·2	4·7	70·5
C5333	o	18·3	19·7	+1·4	11·2	1·2	0·9	10·0	0·5	0·1	0·1	3·5	10·7	1·1	0·8	6·5	19·2
C5343	o	20·0	22·1	+2·2	14·4	2·4	1·5	5·4	0·4	0·1	0·1	1·5	14·0	2·3	1·4	3·9	21·6
C5355	o	25·6	26·0	+0·5	15·2	2·4	1·8	11·2	0·3	0·1	0·1	3·1	14·9	2·3	1·1	8·1	26·5
C5354	o +	24·2	25·3	+1·1	22·4	3·2	1·8	6·7	0·2	0·0	0·1	3·2	22·2	3·2	1·7	3·5	30·7
C5348	o	16·6	17·9	+1·3	11·2	2·4	1·2	4·3	0·1	0·1	0·0	2·3	11·1	2·3	1·2	1·9	16·6
C5835	o	10·4	10·3	−0·1	8·0	0·4	0·6	1·4	0·1	0·0	0·0	0·6	7·9	0·4	0·6	0·7	9·7
C5889	o	6·4	10·6	+4·2	6·4	2·8	0·3	1·0	0·1	0·1	0·0	0·2	6·3	2·7	0·3	0·8	10·1
C6203	o	8·9	11·4	+2·6	8·0	2·4	0·3	1·2	0·2	0·0	0·1	0·3	7·8	2·4	0·2	0·9	11·4

C5835, lower than those obtained by the sodium-acetate method. In the case of soil C5835 the two values may be taken to be equal within the limits of the experimental errors. That the C.E.C. as determined by the sodium-acetate method gives correct figures is supported by the fact that the summation value of the individual cations determined separately approximates more closely to this figure than the figure obtained using ammonium acetate. However, in the eight calcareous soils this was not so. This behaviour is discussed in a subsequent paragraph.

The difference between the C.E.C. as determined by ammonium acetate and that obtained by sodium acetate is ascribed to ammonia fixation in non-exchangeable forms. Bower (1950) showed that some saline and alkali soils of California had appreciable ammonium-fixing capacity and that this capacity varied from 1·8 to 6·1 m.e. per 100 g. of the soil. Rodrigues (1954) had demonstrated that the property of fixing ammonia is also shown by tropical soils. In our studies the ammonium-fixation capacity of the soils ranges from 0·24 to 4·19 m.e. per 100 g. The present knowledge of the subject of ammonium fixation in soils of the semi-arid regions is too meagre to permit any discussion of these figures; but they only stress the importance of utilizing a non-ammonium salt for leaching in determining C.E.C. of such soils.

The values for total exchangeable cations obtained by summing the values for the individual cations compare within experimental errors with the values obtained for the C.E.C. as determined by the sodium-acetate method except in those soils which were calcareous. Since the individual exchangeable cations have been obtained by subtracting the values of such cations in the saturation extract from those in the ammonium-acetate extract, and since for the calcareous soils the total of the individual exchangeable cations does not tally with their C.E.C., it appears that in the calcareous soils the entire quantity of free calcium and magnesium does not come out in the saturation extracts. This behaviour of the calcareous saline and alkali soils of the Indian Gangetic alluvium has already been reported by Agarwal and Yadav (1954). Further, alkaline-earth carbonates are soluble to some extent in normal ammonium-acetate solutions and this fact increases their concentration in such extracts giving higher values for magnesium and calcium (Bower, Reitemeier, and Fireman 1952). After some trials it was found that if calcium and magnesium are determined by Hissink's (1923) method in which use is made of a normal solution of sodium chloride, the summation values of the individual cations approximate more closely to the total C.E.C. as obtained by the sodium-acetate method. Relevant data for the eight calcareous soils in the present study are assembled in Table 3.

(iii) *pH values and exchangeable-sodium percentage.* Fireman and Reeve (1948) observed that the relationship between the pH values of a soil and its exchangeable sodium is not sufficiently close or consistent to be of much diagnostic value in assessing the degree of sodium saturation from the pH value alone. Similar views were expressed by Richards (1950) who states that there does not appear to be any useful general relation between the exchangeable-sodium percentage (E.S.P.) and the

TABLE 3

Exchangeable Cations in the Calcareous Saline and Alkali Soils

Laboratory number	*Exchangeable cations m.e. %*				*Total exch. cations m.e. %*	
	Ca	Mg	K	Na	*By total*	*By* CH_3COONa
C4924	2·8	1·2	0·4	5·4	9·8	10·0
C5770	0·0	0·8	0·0	8·0	8·8	8·6
C4959	3·7	1·6	0·1	5·5	10·9	11·4
C6216	3·2	1·2	1·6	4·9	11·0	11·7
S/C2378	7·8	0·4	1·3	6·8	16·4	16·4
C4967	6·8	1·2	0·7	4·9	13·6	13·7
S/C2405	5·1	0·3	1·2	4·7	11·3	11·3
C5354	14·4	3·0	1·7	3·5	22·7	25·3

pH value of a soil. However, in a later study Fireman and Wadleigh (1951), while undertaking a statistical examination of the analytical records of a large number of soil samples, came to the conclusion that the E.S.P. could be predicted from the pH values, although the exact exchangeable-sodium content of the soils had no such relation. The Handbook (1954) emphasizes the testing of the reliability of this relationship fully before use on any given group of soil samples. Accordingly, the soils in the present study have been utilized to test the adaptability or otherwise of the correlation between the pH values and the E.S.P. for saline and alkali soils of the Indian Gangetic alluvium, the data for which are given in Table 4.

TABLE 4

pH Values and Exchangeable Sodium Percentage

Laboratory number	pH	*Cation exchange capacity by* CH_3COONa *m.e. %*	*Exchangeable* Na *m.e. %*	Na-*saturation* %
C4924	10·9	10·0	5·4	54·1
S/C2361	10·6	12·6	4·4	35·1
C5770	10·5	8·6	8·0	93·1
C4959	10·5	11·4	5·5	48·5
C6216	10·3	11·7	4·9	42·2
S/C2378	10·0	16·4	6·8	41·6
C4967	9·9	13·6	4·9	35·8
S/C2692	9·5	12·0	3·2	27·1
S/C2383	9·3	13·5	2·2	16·4
S/C2405	9·2	11·3	4·7	41·5
C5333	9·0	19·7	6·5	33·1
C5343	8·9	22·1	3·9	17·7
C5355	8·7	26·0	8·1	31·1
C5354	8·2	25·3	3·5	14·0
C5348	8·1	17·9	1·9	10·8
C5835	7·9	10·3	0·7	7·2
C5889	7·8	10·6	0·8	7·4
C6203	7·5	11·4	0·9	7·9

The samples tested have their pH values spread over a range usually encountered in Uttar Pradesh and the corresponding values for the

percentage of exchangeable sodium also vary over a wide range. The data recorded in Table 4 were plotted on a graph (Fig. 2) and the usual correlation coefficient between the pH values and E.S.P. was worked out. It is evident from the graph that a fair degree of correlation exists between these two values, the correlation coefficient being 0·806 which is

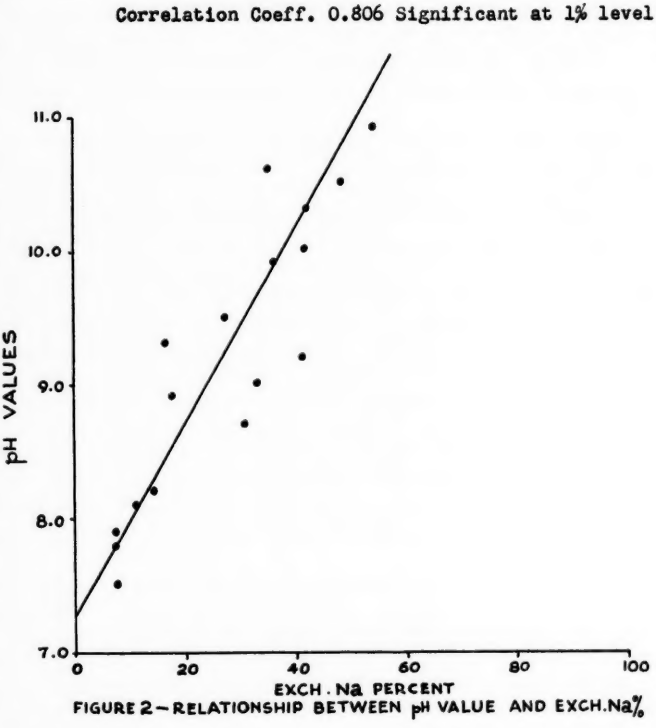

FIGURE 2—RELATIONSHIP BETWEEN pH VALUE AND EXCH.Na%

significant at 1·0 per cent. level. The points lie very close to the line of regression with the only exception of one sample (C5770) which had a very high salt content and showed considerably lower pH value in comparison to its exchangeable-sodium percentage. The relationship does not seem to be much affected by lower salt contents up to 40 millimhos per cm., nor has the presence of free lime any modifying effect. Fireman and Wadleigh (1951) also observed that the presence of salts had a relatively minor effect, although that of gypsum caused great variation of the generalized relation between pH and E.S.P. Since in our soils the presence of gypsum is insignificant (Agarwal and Yadav, 1954), its effect is practically negligible. In the American soils studied by Fireman and Wadleigh (1951) it was found that the degree of validity in the prediction of E.S.P. values from the pH determinations was not very precise, for they state that only 44 per cent. variance in pH can be

explained by the corresponding variations in E.S.P. and that for a particular pH value the value for E.S.P. may vary from 17 to 50 per cent. However, in the data for the Gangetic alluvium recorded by us the degree of precision appears to be much closer. The range of prediction in our soils is within $\pm 0{\cdot}5$ pH units and accordingly, under field conditions an estimate of the pH values can give an idea of the probable E.S.P. within ± 7–8 units. With the limited data our tentative limits appear to be (1) pH values varying from 7·0 to 8·2 perhaps indicate an E.S.P. of 0 to 15, (2) pH values from 8·2 to 10·0 may have an E.S.P. of 15 to 40, and (3) pH values over 10·0 may have an E.S.P. ranging from 40 to 100.

(iv) *Soluble cations and exchangeable cations.* No fully satisfactory and universal laws governing the cationic equilibrium between the soil solution and the base-exchange complex have yet been developed. However, workers at the U.S. Salinity Laboratory consider that Gapon's equation can give a workable relationship to characterize the equilibrium in respect of the cations in the saturation extract and those in the base-exchange complex for the saline and alkali soils (Handbook, 1954). This relationship is of importance in diagnosing the saline and alkali soils, since it enables an appraisal of the exchangeable-sodium percentage from the values for the total soluble cations and soluble-sodium percentage in the saturation extracts. With the limited number of samples used by us an attempt was made to see if these relationships also exist in our soils and whether Gapon's equation can give a constant which can be utilized for calculating the exchangeable-sodium percentage from the results of cation analyses in the saturation extracts. Pertinent data calculated from the foregoing tables in this respect for the eighteen soil samples studied are given in Table 5.

The figures for Gapon's constant vary considerably, but the average value for the constant, namely 0·026, has been used to calculate the exchangeable-sodium percentage by using the formula given by the U.S. Salinity Laboratory workers. The figures so obtained have been compared with those got experimentally by using the sodium-acetate method. A scrutiny of the data shows that there is a considerable and sometimes very large variation between the two sets of figures. Out of the 18 soil samples used in this study only 8 (i.e. 44 per cent. of the total) showed a variation of 5 units between the calculated and experimental values, 3 showed a variation of 10 units, and 7 above 10 units. It appears, therefore, although tentatively, that the determination of the exchangeable-sodium percentage by the use of Gapon's equation for the soils in question cannot give a very valid estimate and that only in 44 per cent. of the cases the chances are that the two values may be within 5 units of variance.

Recently a ratio, designated as the sodium-adsorption ratio (S.A.R.), has been used to discuss the equilibrium between the soluble and exchangeable cations in saline and alkali soils (Handbook, 1954). The S.A.R. has been defined as $Na^{+}/\sqrt{(Ca^{++}+Mg^{++})/2}$ where the figures represent the concentration in m.e. per litre of the respective cations in the saturation extract. The relationship between the S.A.R. and the ratio between

the exchangeable sodium and C.E.C. minus the exchangeable sodium (E.S.) for 59 American soils was found to be linear and it has, therefore, been assumed that this correlation is sufficiently close to enable the practical use of the relations. It is of interest to see if such relationship

TABLE 5

Relation between Soluble and Exchangeable Cations

Laboratory number	*Gapon's constant* $\frac{\sqrt{(Ca^{++}+Mg^{++})/2}}{Na^{+}} \times \frac{Na^{+}}{Ca^{++}+Mg^{++}} = Kg$	*Percentage exch. Na saturation*		*Sodium-absorption ratio* $\frac{Na^{+}}{\sqrt{(Ca^{++}+Mg^{++})/2}}$	*Exchangeable-sodium ratio* $\frac{E.S.}{(C.E.C.-E.S.)}$
		Determined by CH_3COONa	*Calculated by the equation* *		
C4924	0·02	54·0	61·9	67·4	1·2
S/C2361	0·04	35·1	24·1	15·9	0·5
C5770	0·03	93·1	89·7	345·3	13·4
C4959	0·02	48·5	59·1	64·0	0·9
C6216	0·05	42·2	34·2	24·1	0·7
S/C2378	0·00	41·6	81·2	201·9	0·7
C4967	0·03	35·8	27·4	17·1	0·6
S/C2692	0·02	27·1	31·3	19·1	0·4
S/C2383	0·03	16·4	18·6	9·7	0·2
S/C2405	0·08	41·4	21·1	10·9	0·7
C5333	0·02	33·1	34·0	21·1	0·5
C5343	0·02	17·7	18·6	9·6	0·2
C5355	0·02	31·2	35·6	23·3	0·4
C5354	0·01	14·0	44·8	35·9	0·3
C5348	0·04	10·8	47·9	37·5	0·1
C5835	0·01	7·2	30·6	17·1	0·1
C5889	0·02	7·4	8·6	4·0	0·1
C6203	0·02	7·9	8·9	4·3	0·1

* $\sqrt{\left(\frac{50(100-\text{S.S.P.})}{(\text{S.S.P.})^2 \times \text{T.S.C.}}\right)} \times \frac{\text{E.S.P.}}{100-\text{E.S.P.}} = 0{\cdot}026.$

also exists for our soils, for it would enable determination of the exchangeable-sodium ratio from a simple consideration of cationic contents of the saturation extracts. The available data, for which the exchangeable-sodium ratio is not more than 1·0, have, therefore, been plotted against the corresponding S.A.R. values in Fig. 3, an examination of which indicates that the points falling near the line are only about 50 per cent. of the total number of the samples examined. The correlation coefficient works out at 0·516 which is significant at 5 per cent. level. The available evidence shows that the relationship proposed, which is based essentially on the validity of Gapon's equation, does not hold universally and only in about 50 per cent. of the cases the chances are that the correct values for the exchangeable-sodium ratio or the exchangeable-sodium percentage can be obtained from the data on cationic contents of the saturation extracts. Much further work on different groups of soils needs to be done before any satisfactory relationship of universal applicability could perhaps be found.

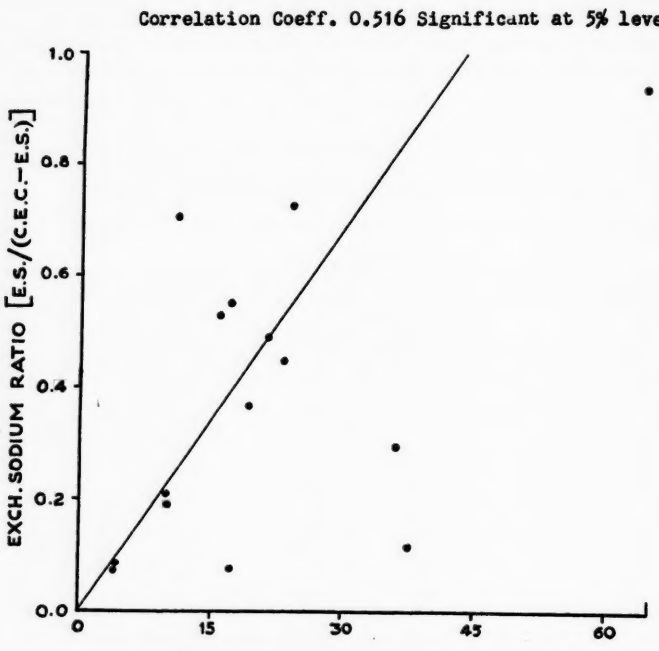

FIGURE 3-RELATIONSHIP BETWEEN S.A.R. AND EXCH. Na-RATIO

Summary and Conclusions

An attempt has been made to determine whether the diagnostic techniques for saline and alkali soils proposed for the American soils can be used for similar soils on the Indian Gangetic alluvium developed under entirely different climatic and environmental conditions.

For the chemical measurements recommended a good and workable correlation existed between the electrical conductivity of the saturation extracts of the soils and their total cationic contents in milli-equivalents per litre. In the case of cation-exchange capacity it was found that the sodium-acetate method of Bower *et al.* gives a value which more closely approximates to the total of the individual exchangeable cations determined separately for non-calcareous soils. Hissink's method gives a better appraisal of the figures for exchangeable calcium and magnesium in soils which are calcareous. A fair degree of correlation was found to exist between pH values and the exchangeable-sodium percentages of soils. It appeared from these studies that, unlike the American soils, the determination of the exchangeable-sodium percentage using Gapon's equation which is based on the relationship existing between the soluble

and exchangeable cations, or directly from the sodium-absorption ratios, cannot give correct estimates for the Indian soils.

In conclusion it is evident that the pH value, electrical conductivity of saturation extracts, cation-exchange capacity using sodium acetate, and the degree of calcareousness of the samples should form workable criteria for salinity and alkali appraisal of Indian Gangetic alluvial soils. These determinations can, therefore, be used as a basis for mapping alkali soils in any large-scale soil-survey operations in the above or similar areas where salts or alkali may be a problem.

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SILICA PARTICLES IN SOME BRITISH SOILS

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WITH ONE PLATE

Introduction

MINERAL crystals of the silica group are so abundant and widespread in the earth's crust and its weathering products that a statement of their presence in a particular soil is often of little help in deciding the source of its mineral fraction. Nevertheless, if the microscopical examination of the silica minerals leads to a precise knowledge of the species or variety, shape and size of particles, or other details, this information will often provide suggestive and sometimes conclusive evidence of their origin and add much to an understanding of the history of the soil as a whole. Deductions of this kind may often be made most readily from a study of the heavy minerals, but in the case of limestones the heavy fractions are often so small that evidence provided by the silica minerals may be the only reliable link between soil and parent rock.

Silica (silicon dioxide, SiO_2) can occur in at least three completely different crystalline forms of which two, tridymite and cristobalite, are relatively scarce in the earth's crust. Quartz, the commonest form, has a great many varieties but for the practical study of soil particles only two categories need be considered:

(*a*) In the first category the particles consist normally of one crystal or part of one crystal, so that it is possible to determine completely the optical properties of the mineral. Such particles will be spoken of as ordinary quartz.

(*b*) In the second, the particles are aggregations of many individuals each having optical properties, so far as they can be determined on such small objects, similar to those of quartz, though it has remained for X-ray work to prove that they have the crystal structure of this mineral. Such material is commonly spoken of as flint when associated with chalk, and chert when associated with well-consolidated limestones. These and other varieties of crypto-crystalline quartz are classed together as chalcedony.

There are also hydrated forms of silica ($SiO_2.nH_2O$), spoken of comprehensively as opaline silica. These differ from quartz and chalcedony in being definitely non-crystalline and having lower densities and refractive indices (Table 1). All silica secreted by living organisms appears to consist initially of the opaline variety.

Van Rummelen (1953) has described isotropic silica occurring in Indonesian soils and considers it to have been deposited inorganically round rootlets or in old root channels. In New Zealand soils Fieldes and Swindale (1954) have found a variety of silica (tentatively named chalcedonite) resembling chalcedony but having a lower refractive index.

Ordinary Quartz

Examination of a simple quartz grain under a microscope, using crossed polars and white light, shows that all its parts are in the same optical orientation; that is to say, if part of it is dark then the whole is dark, and if part transmits light to the eye then the whole does so. Without crossed polars a clean grain of quartz shows only a feeble outline when mounted in Canada balsam, but with crossed polars the shape of all quartz grains, except those which have their optic axes perpendicular to the slide, can be made evident; and the banding in Newton's scale of colours, by indicating the thickness for each optical

TABLE I

The Properties of some Forms of Silica and Mounting Media

	Specific gravity	*Mean refractive index*	*Birefringence*	*Water content*
Quartz	2·65	1·55	0·009	nil
Chert and flint	2·62	1·55	0·009	trace
Opaline silica	*c.* 2·15	1·43	nil	up to 10%
Canada balsam	..	1·54	..	..
Water	..	1·33	..	..

path, will give further information about the shape of the grain (Plate I A, &c.).

Quartz has no crystallographic cleavage, but breaks somewhat in the manner of glass, giving particles with sharp edges and points but no plane surfaces, and under sedentary conditions these features may be retained almost indefinitely. On the other hand, if the particles are transported they slowly abrade one another and become more and more rounded. As a result of this, quartz grains showing an appreciable degree of rounding are common in most sands and sandstones. They are also found in the sand fractions of some boulder clays and in soils in much of the country which was subjected to Pleistocene glaciation even in places where one might expect quartz to be present only as unabraded fragments (e.g. in soils on granite) or to be completely absent from the sand-size fraction (e.g. in soils on shale, chalk, and pure limestone). The writer has described and figured examples of these phenomena in an earlier paper on the soils of North Wales (Smithson, 1953), including cases of soils which have generally been regarded as derived from Carboniferous Limestone. Two suggestions emerge from evidence of this nature. Firstly, that the microscopic examinations of soils is capable of indicating traces of glacially transported material which are not obvious from field studies and would not be shown on an ordinary Drift map; and secondly, that although the erosive action of ice moving over a resistant rock is to produce angular fragments or rock-flour, yet its action upon weakly cemented sandstone will be very different, in that

the sand grains may be detached, transported, and redeposited with no appreciable change of size or shape.

Two quartz particles from a soil which has been mapped as the Pentraeth Series (defined as one of the soils developed on drift consisting of Carboniferous Limestone) are shown in Plate I A and B, as seen between crossed polars. In A the outline and the curved form of the dark bands indicate that the grain has, at some stage, been well rounded by transport and may in this condition have formed part of a sandstone or arenaceous limestone within the Carboniferous Limestone formation, though there is also the possibility that its presence in the soil may be due to contamination from an arenaceous deposit belonging to some other stratigraphical formation (e.g. the Triassic sandstones). The quartz particle B, similar to many which can be obtained by dissolving the local limestones in acid, is a well-shaped quartz crystal as can be seen from the central rectangle (grey in the photograph) which marks the position of one of the faces of the hexagonal prism, and from the well-defined bands, particularly in the bottom left of the picture, where they portray a well-shaped pyramidal termination. Crystals of this kind are scarce in the soil and their presence does no more than show that the insoluble residue of the limestone makes a trivial contribution to the depth of this soil.

Well-shaped crystals of quartz appear to have formed in many limestones during consolidation. In some sandstones also, quartz has developed under similar conditions, but in these rocks the newly crystallized material usually grows on quartz grains already present, attaching itself in optical continuity with these original grains and forming true crystal faces wherever space allows. These facetted grains are readily detected in soils derived from this type of sandstone. Plate I C and D show a quartz grain from a soil in Northumberland as seen with ordinary light and with crossed polars respectively. The original grain had some impurity on its surface and this causes the original shape to be seen clearly when ordinary light is used, but under these conditions the quartz which has been added later and has a clean surface in contact with the Canada balsam is almost invisible. Using crossed polars, however, the true outline of the new facettes is clearly seen.

Chalcedony

A chert or flint grain, being an aggregate of minute particles of quartz, each one oriented differently from its neighbours, appears between crossed polars as a speckled object (Plate I E). The size of each component particle is usually such that it gives only a first order grey or white of Newton's scale and none of the brighter colours exhibited by an ordinary quartz sand grain. Moreover, in whatever position the chert or flint grain is oriented on the slide, some of the component particles will be light and some dark when viewed between crossed polars, and there will be no position in which the whole grain is dark as there is in the case of the simple grain of quartz. The micro-structure of chert and flint can also be seen by means of the phase-contrast microscope (Smithson, 1953, Plate III D).

Although chert and flint occur in beds or lumps of considerable size, such material may be reduced by fracture and abrasion to particles of sand-grain size. Their manner of breaking does not differ greatly from that of quartz, but abrasion during transport appears to be less efficient in rounding them. Microscopically there is no clear distinction between fragmental chert and flint. Where the nearest or most probable source of the grains is the siliceous beds associated with the Carboniferous Limestone the mineral may be referred to as chert, although similar grains met with in the Tertiary deposits of south-east England and in soils derived from them, being originally derived for the most part from the chalk, may be referred to more appropriately as flint.

Some of the chert and flint particles found in the insoluble residues of limestone and chalk or in the sand fractions of soils are not in the form of fragments produced by the breaking up of large masses of these minerals. Some of the chert particles obtained by dissolving limestones in acid appear to have grown in the rock and are somewhat moss-like though there is no evidence that any organic agency is responsible for their shape (Smithson, 1953, Plate III D and E). Others exhibit the shapes of the hard parts of organisms, and by studying micro-fossils of this kind it is often possible to trace the parentage of a soil with a fair degree of certainty. There is often biological evidence that the material originally secreted was calcium carbonate (calcite or aragonite) which has been subsequently replaced by silica. In other cases the hard parts of the organisms are known to have consisted originally of opaline silica which with the passage of time has become converted into its present anhydrous form.

It has been pointed out that in the heavily glaciated country of North Wales, siliceous micro-fossils which would be expected to be released by the weathering of the Carboniferous Limestone are scarce in the soils in the limestone districts (Smithson, 1953). Single-rod sponge spicules are, however, met with occasionally in these soils (Plate I F) and in one Anglesey soil sample silicified encrinite disks have been found to be fairly common (Smithson, 1954). In the south of England the Portland Stone (a Jurassic limestone) has long been known to contain sponge spicules of the genus *Pachastrella* (Woodward, 1895). Four-armed spicules belonging to this or some related genus have been found to be plentiful in the sand fraction of a soil resting on Portland Stone near St. Albans Head in Dorset (Fig. 1 and Plate I G and H). This locality is well beyond the limit of Pleistocene glaciation, there is no microscopical evidence of the influx of drift and the soil in question appears to be a genuine example of a soil formed by the solution of this particular limestone. Another striking example of a soil containing micro-fossils of Jurassic age is found on rocks of the Corallian formation lying to the north of the Vale of Pickering in Yorkshire. In the calcareous grits and oolitic limestones of this formation the remains of the sponge *Rhaxella perforata* are extremely abundant (Wilson, 1933, 1949). The siliceous parts of this sponge were small ovoid bodies of fairly uniform size, *c.* 150 μ, which since they correspond to the rod-like bodies in other sponges are technically described as spicules. When some of the

calcareous grits are dissolved in hydrochloric acid it is found that in the insoluble residue most of the particles of sand-grain size consist of these spicules, and in a soil developed on one of these beds it was found that they formed the greater part of the sand fraction (Plate I 1). That this soil is a residual one is shown not only by the abundance of *Rhaxella*

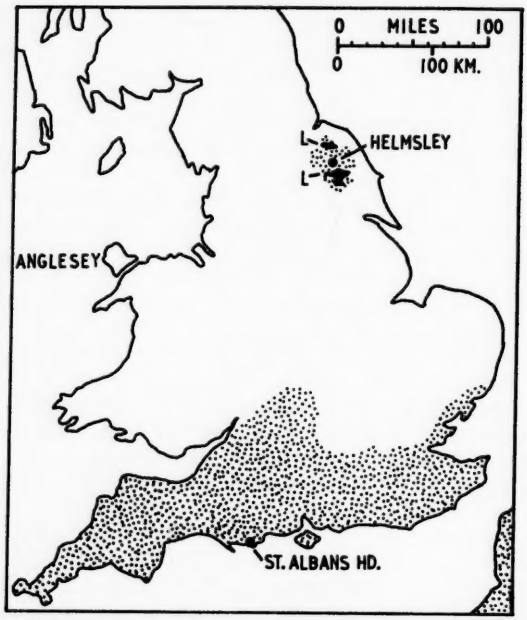

FIG. 1. Relation of cited limestone localities to Pleistocene glaciation. Stippled: Regions not traversed by the ice-sheet. L.L. Glacial lakes of Eskdale and the Vale of Pickering. After W. B. Wright (1937) and P. F. Kendall (1902).

spicules, but also by the nature of the heavy mineral assemblage which gives no evidence of any contamination by glacial drift. This is in keeping with the accepted view that most of the country between Eskdale and the Vale of Pickering, two east–west valleys which were occupied by lakes in glacial times, was never traversed by ice, though lying well to the north of the southernmost limit of the ice-sheet (Fig. 1).

Opaline Silica

Since opaline silica tends to lose its water in a relatively short time (geologically speaking) it is usually safe to assume in dealing with soil particles that any small siliceous organic remains which consist of chert or flint will be micro-fossils from the parent rock and that any which consist of opaline silica will be the remains of recently living organisms. Sometimes the latter are so abundant that they can be detected without

any elaborate preparation of the soil specimen. For this purpose use has been made of a device which was prepared for the field study of dickitic rocks and soils and consisted of the barrel of an old microscope adapted as follows. A metal tube was made to screw on to the bottom of the barrel and within this tube there was fitted a second tube carrying a glass disk to act both as stage and object slip. Rough focusing was done by sliding this stage-tube, but the barrel possessed a fine adjustment adequate for the $\times 45$ objective. This instrument being held like a telescope, the sky served as a light source. A small pinch of the topsoil was mixed with a little water and a portion of this transferred to the glass disk and then protected by a small cover glass for microscopic examination. For laboratory study the soil was cleaned with hydrogen peroxide and after fine sieving and sedimentation most of the opaline silica particles were found in the silt fractions. There would appear to be a sufficient specific gravity difference for a separation of opaline silica from other kinds of silica by means of a suitable heavy liquid (Table 1) but in practice separation is imperfect owing to surface tension troubles. Nevertheless, if a liquid with a specific gravity of about 2·4 is used as a temporary mounting medium any quartz and chert particles will rest on the slide and the opaline silica particles will float in contact with the cover glass, so that by racking up the microscope it is possible to arrange that only the opaline variety is seen clearly in focus. Opaline silica can also be recognized by its being isotropic, i.e. it remains dark between crossed polars, and by its giving a bold outline when mounted in Canada balsam, since its refractive index is so much lower than that of the mounting medium.

These small bodies are of many different kinds but most of them fall into one or other of two categories, (*a*) silica which has formed an essential part of a small organism, or (*b*) silica which has formed a minor part of a larger organism.

(*a*) Diatoms, for example, make use of silica to create an essential protection and support for the whole organism, secreting it in the form of valves which periodically separate in their process of cell multiplication. Thus diatom remains may be in the shape of the complete organism, of separate but unbroken valves (Plate I J) or the broken fragments of valves (Plate I K). They may be relatively large as in Plate I J where the valve measures about 150 μ, or very small as in Plate I L.

The fresh water diatoms inhabit lakes and marshes, and species which live in these places also live in the capillary water of soils. In addition to the moisture conditions necessary for the survival of these organisms there must be silica available in solution. Although the amount needed is small it is unlikely that this need can be met by the solution of any form of 'free silica' particles and a more probable source would appear to be the decomposition of felspars and other silicate minerals. There does not appear to be sufficient data, however, to show whether soils richest in weatherable silicate minerals tend to have the largest diatom populations.

Though capable of living in such apparently diverse habitats as open lakes and soil pores the diatoms are rather susceptible to changes in

acidity and each species thrives only within its characteristic pH range (Hustedt, 1937–8; Woodhead and Tweed, 1954). It is conceivable, therefore, that diatom remains should be capable of indicating any major differences between past and present pH conditions of a soil.

(*b*) Some of the larger plants secrete opaline silica which serves as no more than a reinforcement for minor structures. When the plant or its parts wither to become incorporated in the soil and gradually decompose, the silica in the shape of minute rods, hooks, spines, &c. is released apparently unaltered (Plate I L, M, N, and O). Such bodies are present in grasses, sedges, and many other kinds of plants (Netolitzky, 1929). Little work appears to have been carried out on the occurrence in soils of these interesting objects and it is possible that they might, with careful study, provide information about the former vegetation and soil conditions of the sites where they occur.

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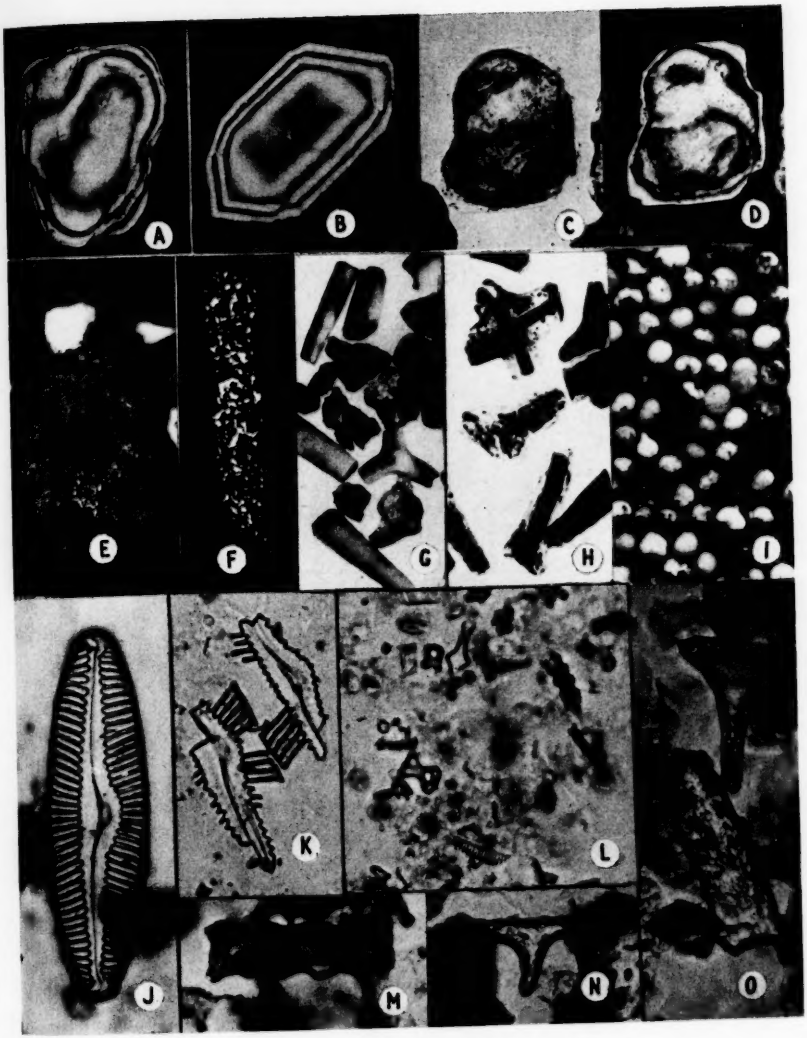

F. SMITHSON—PLATE I

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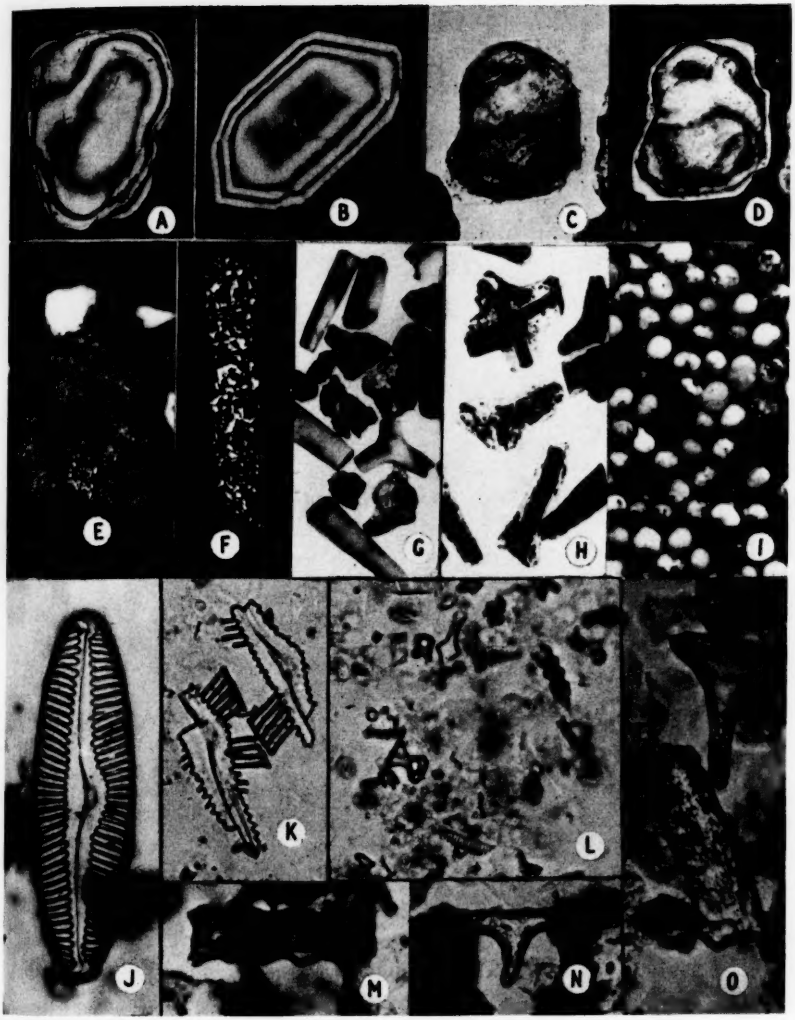

F. SMITHSON—PLATE I

KEY TO PLATE I

All material mounted in Canada balsam except G and I. Photographs with crossed polars were all taken with monochromatic light, which gives the clearest picture for an uncoloured illustration.

Ordinary Quartz

A. Rounded grain from soil on glacial drift derived from Carboniferous Limestone, &c. (Pentraeth Series), Llanbedr-Goch, Anglesey (Soil Survey Sample S. 347). Crossed polars, × 80.

B. Euhedral crystal from same sample as A. Crossed polars, × 80.

C. Rounded grain with euhedral secondary growth. From soil on Rothley Grit (Carboniferous), Rothley Crags, Northumberland. Ordinary light, × 50.

D. Same grain as C. Crossed polars, × 50.

Chert

E. Angular grain from soil of mixed glacial drift with Carboniferous Limestone predominating, Glen of Aherlow, Co. Tipperary, Eire. Crossed polars, × 80.

F. Sponge spicule from same sample as A. Crossed polars, × 80.

G. Sand fraction rich in sponge spicules from soil on Portland Stone, near St. Albans Head, Dorset. In air, × 36.

H. Sponge spicules from same sample as G. × 48.

I. Sand fraction consisting chiefly of oval spicules of the sponge *Rhaxella perforata*, from soil on a Lower Corallian limestone, near Helmsley, Yorkshire. In air, × 32.

Opaline Silica

J–O are all from a soil on Millstone Grit, Slaley, Northumberland. × 380.

J. A complete diatom valve (*Pinnularia, distantes* group).

K. Fragments of *Pinnularia*.

L. Small silica bodies (fragments of diatoms, &c.).

M, N, O. Silica bodies probably derived from unidentified plants.

ION-EXCHANGE PHENOMENA IN SOME SOILS CONTAINING AMORPHOUS MINERAL CONSTITUENTS

K. S. BIRRELL AND M. GRADWELL

(*Soil Bureau, Department of Scientific and Industrial Research, New Zealand*)

(Soil Bureau Publication No. 69)

Summary

Soils containing allophane, 'palagonite', and amorphous oxides have been found to give cation-exchange capacity values as determined by conventional methods, which depend markedly upon concentration of leaching solution, the cation in the solution, the volume of the washing alcohol, and its water content. Experiments in which the soil is brought to equilibrium with solutions of barium acetate adjusted to pH 7, and containing an excess of barium with respect to the cation-exchange capacity value given by the leaching method, indicate that the uptake of cation conforms to the Brunauer, Emmett, and Teller theory of multi-layer physical adsorption. Similar results are also given by barium-chloride and lithium-acetate solutions at pH 7. Adsorption does not take place in the absence of water, and it is thought that it is the hydrated cation which is effective in covering the surface. Adsorption is strongly influenced by equilibrium pH values of the solutions. The adsorption of cations by these soils closely resembles the behaviour of hydrated alumina prepared by precipitation from sodium aluminate with CO_2. The acetate and chloride anions are taken up to a much smaller extent than the cations. Titration experiments indicate that soils containing allophane exhibit little if any tendency to hold exchangeable hydrogen ions in the same manner as montmorillonite.

Introduction

In the course of an examination of volcanic ash soils containing the amorphous mineral allophane (Birrell and Fieldes, 1952), it was noted that a high exchange capacity for the cations NH_4^+, Na^+, K^+, and Ba^{++} appeared to be associated with the presence of this substance. It was also noted that these cations were fairly easily removed from the soils by leaching with water. Subsequently, it was also found that the substitution of 2 N solutions of ammonium acetate for N solutions in the standard laboratory determination of cation-exchange capacity (C.E.C.) used in the Soil Bureau (Metson, 1955) (in which the ammonia taken up by the soils is, after removing excess ammonium acetate with alcohol, estimated by distillation into standard acid) gave appreciably higher values. These facts seemed sufficiently different from those to be expected if the mechanism was the normal cation exchange shown by the crystalline clay minerals, to justify investigation. In addition to New Zealand volcanic ash soils known to contain much allophane, there were examined also some lateritic soils which showed high apparent cation-exchange capacity in the absence of crystalline clay minerals of known high exchange capacity.

Description of Soils

1. Volcanic ash soils having allophane as a major constituent of the clay fraction.

(*a*) S447A and S503. Subsoils from Whenuapai Airfield, yielding about 60 per cent. of fraction below 2μ diameter.

(*b*) S479. Subsoil of Tirau Ash Shower from Whakamaru Hydro-electric Station site, yielding about 20 per cent. below 2 μ diameter.

(*c*) S311. Subsoil of Egmont Ash, from the grounds of New Plymouth Hospital, yielding also about 20 per cent. below 2 μ diameter.

In (*a*) and (*b*) only small amounts of kaolin and quartz in addition to allophane could be identified by X-ray and differential thermal analysis (D.T.A.) in the clay fraction. The clay fraction of (*c*) contained about equal parts of allophane and halloysite. Dispersion of soils for preparation of clay fractions was effected with sodium hydroxide at about pH 10, the organic-matter content being negligible. No deferration of the soil was attempted, in view of the risk of attacking the allophane (Birrell and Fieldes, 1952). It was unlikely that all the allophane was present in the clay fraction because the silt fraction of S479 was found to possess about 40 per cent. of the apparent cation-exchange capacity of the clay fraction, when this quantity was determined by the routine procedure.

2. Lateritic soils having hydrous oxides or 'palagonite' as the major constituent.

(*a*) 1390B. Subsoil from Brown Loam soil group, Whangarei County. D.T.A. shows that mainly kaolin and limonite are present, with no detectable amounts of high exchange-capacity minerals.

(*b*) 5810. Aitutaki Island, Cook Islands. This soil, containing mostly amorphous oxides, has been described by Fieldes, Swindale, and Richardson (1952).

(*c*) 6168. Aitutaki Island. This soil was reported to contain the amorphous iron-aluminium silicate 'palagonite' (Dominion Laboratory, 1953). A light fraction (S.G. 2·2–2·3) separated from this soil had a cation-exchange capacity of 0·94 m.e. per gramme when neutral 2 N ammonium acetate was used in the standard method.

3. In addition a synthetic hydrated alumina, supplied by Mr. M. Fieldes, Soil Bureau, and prepared as described by Fieldes *et al.* (1952) was examined.

A characteristic of all these materials is a high surface area as shown in Table 5. This was determined by the adsorption of nitrogen at $-183°$ C. using the technique of Makower, Shaw, and Alexander (1937). The apparatus used enabled values of P/P_0 (relative pressure) up to 0·2 to be reached. For the Whakamaru soil clay fraction, check runs with argon at the same temperature (maximum P/P_0 value reached = 0·7) gave surface-area values within 5 per cent. of the nitrogen value. Application of the adjustment method of Joyner, Weinberger, and Montgomery

(1945) to the argon results indicated a value for the constant n in the general adsorption equation of Brunauer, Emmett, and Teller (B.E.T.) (1938) of at least 4·0, thus justifying the use of the simplified B.E.T. equation:

$$\frac{P}{V(P_0-P)} = \frac{1}{V_m C} + \frac{(C-1)P}{V_m C P_0} \quad \text{(which holds when } n = \infty\text{)}$$

for calculating surface areas from the nitrogen adsorption data.

Experimental

Cation-exchange capacity determinations by the leaching method were carried out with the apparatus described by Metson (1955), and using slight modifications of his procedure. In this, air-dry soil (10 g.) is leached first with neutral N ammonium acetate (350 ml.) and then with 80 per cent. alcohol (250 ml.) containing 0·5 ml. 2 N ammonium hydroxide per litre. All salt solutions were adjusted to pH 7·0 before use in this investigation. A suspension of magnesium oxide was used for liberating the ammonia taken up from ammonium-acetate solutions. When barium acetate was used in leaching-tube experiments the excess was removed by washing with plain 80 per cent. alcohol, the barium displaced with N acetic acid, and subsequently determined as sulphate.

For the equilibrium experiments, weighed amounts of air-dried material were added to accurately measured volumes of salt solutions. Tests at 20° C. were made in stoppered flasks, those at 95° C. in sealed tubes. Desorption tests were carried out by adding known volumes of water to the suspensions at equilibrium, and bringing to equilibrium again. Shaking intermittently over a period of 24 hours or continuously for 1 hour was found to be sufficient to attain equilibrium. After centrifuging for 10 min. the uptake of cation or anion was found by analysis of the supernatant liquid. Barium and lithium were determined gravimetrically as sulphate, acetate by distillation with sulphuric acid and titration of the distillate, chloride by titration with mercuric nitrate using diphenyl carbazone as indicator.

Solubilities of the salts used were determined on a weight/volume-of-solution basis, values found being:

Barium acetate	20° C.; 4·45	m.e.	per ml.
„ „	95° C.; 4·61	„	„
„ chloride,	20° C.; 3·20	„	„
„ „	95° C.; 4·98	„	„
Lithium acetate,	20° C.; 5·8	„	„

Cation-exchange Capacity by Leaching Procedure

The results of these experiments are shown in Tables 1, 2, and 3. The departures from the standard procedure made in the course of these tests, which are apparent from the tables, are not considered to invalidate the results. For the Whenuapai soil, the washing alcohol was of 80 per cent. strength, adjusted to the neutral point of brom-thymol blue with ammonia as specified by Schollenberger and Simon (1945), but for all

other materials alcohol of 95 per cent. strength was used without the addition of ammonia as recommended by Shaw (1940). Sections (*a*) and (*b*) of Tables 1 and 2 show that the cation-exchange capacity of these soils increases with increasing concentration of ammonium-acetate leaching solution, provided that the volume of washing alcohol relative to the amount of soil taken is constant. The change in C.E.C. is less marked with the lateritic soils than with the allophane soils. Illite and Wyoming bentonite showed no appreciable change in C.E.C. with changes in concentration of ammonium-acetate solution using the same analytical procedure, provided sufficient was present to saturate the exchange complex.

Increasing the relative volume of washing alcohol gives lower results, and if, as is shown by the footnote to Table 2, alcohol is replaced by water as washing medium, much lower results are obtained. It appears that the exchange complex in these soils must be extremely easily hydrolysed.

Table 3 shows that leaching the soil first with a strong solution of ammonium acetate, followed by a weaker solution, reduces the cation-exchange capacity to approximately the value which would have been obtained using the weaker solution originally, and if the second leaching is made with water, the C.E.C. is lowered still further.

When barium acetate was used in these experiments, the more concentrated the solution, the higher the C.E.C. value obtained, and the level of the values was greater than for ammonium acetate. Sodium acetate gave a lower level of C.E.C. values than ammonium acetate.

Equilibrium Experiments

The foregoing facts, namely, dependence of C.E.C. value on strength of leaching solution, ease of hydrolysis of the exchange complex, and variation in C.E.C. value with different cations, indicated some kind of adsorption mechanism rather than normal base exchange occurring with these soils, and it was accordingly determined to carry out equilibrium tests at constant temperature.

From these, the relationship of x/m, the amount of cation taken up per gramme to C, the equilibrium concentration was obtained. In Figs. 1 *a* and *b* and 2 *a*, x/m is shown plotted against C/C_0, where C_0 is the solubility of the salt used at the temperature of the experiment. For all soils and clay fractions tested, as well as for the synthetic hydrated alumina, the resulting curves resemble portions of gas adsorption isotherms.

A parallel experiment with a sample of calcium-saturated bentonite brought to equilibrium with barium-acetate solutions gave on the other hand an uptake of barium ion which was independent of equilibrium concentration (Fig. 1 *a*). The uptake of barium ion in this case agrees with the C.E.C. value obtained by Dr. R. B. Miller of Soil Bureau using the standard ammonium-acetate leaching procedure.

Neither the Freundlich nor the Langmuir adsorption equations were applicable to the results of the equilibrium experiments mentioned.

However, Ewing and Liu (1953), who recently studied the adsorption of the ionic dyes Crystal Violet and Orange II on certain pigments,

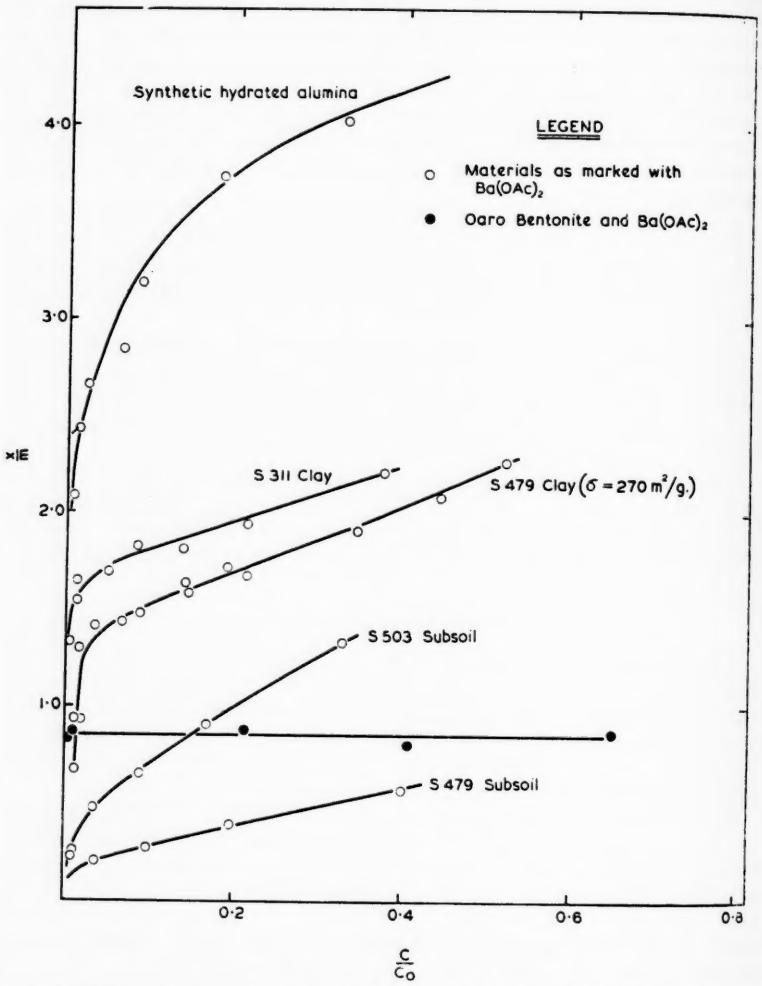

FIG. 1 (*a*) Adsorption isotherms of barium ion at 20° C. for soils and clay fractions, containing allophane, and for hydrated alumina.

found that, although these particular equations were likewise not applicable to their results, a modification of the multilayer B.E.T. gas-adsorption theory in which the reduced pressure P/P_0 was replaced by the reduced concentration C/C_0 and the volume adsorbed (v) was replaced by the amount adsorbed per gramme (x/m), for the case in which the

constant $n = \infty$, was satisfactory for values of C/C_0 up to 0·25. That is to say, the B.E.T. equation quoted earlier, according to Ewing and Liu, can be written as:

$$\frac{C}{x/m(C_0-C)} = \frac{1}{(x/m)_m K} + \frac{K-1}{(x/m)_m K} \cdot \frac{C}{C_0}$$

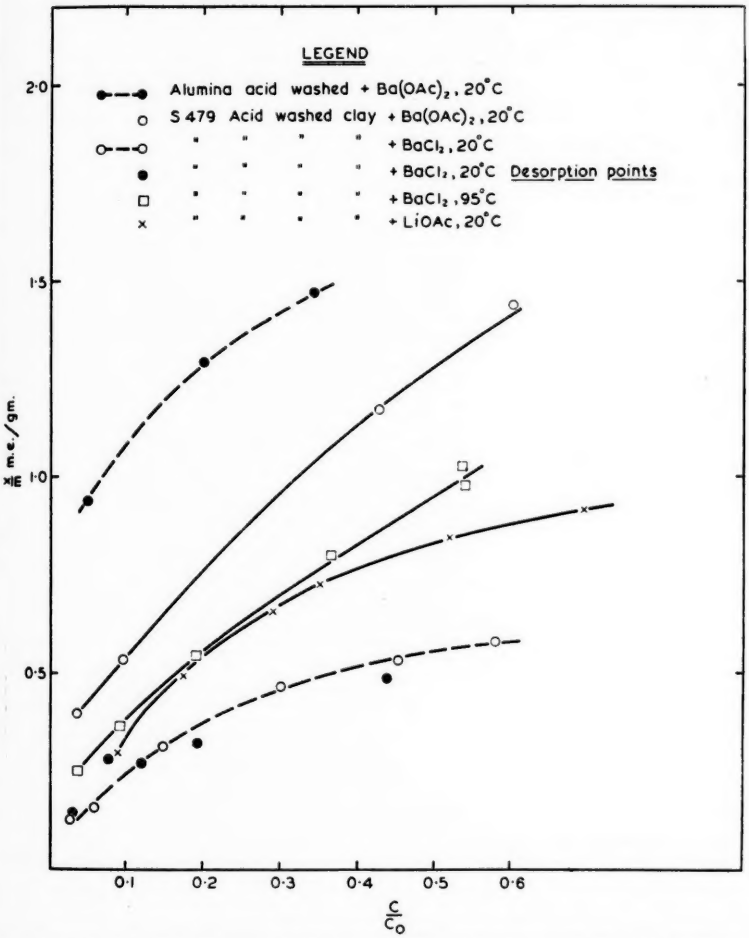

FIG. 1 (*b*) Adsorption isotherms of barium and lithium ions for acid-washed samples.

for adsorption from solution, where the constant K replaces constant C of the B.E.T. equation for the sake of clarity. (It should be noted that a misprint in their paper omits K from the denominator of the second term on the right-hand side.)

The linearity of the plot of $\frac{C}{(C_0-C)x/m}$ against C/C_0 for the allophane clay fractions shown in Fig. 1 *c* indicates that the above equation fits the uptake of cation by this substance. The synthetic alumina fits fairly well also. For conditions of lesser adsorption such as obtained with the

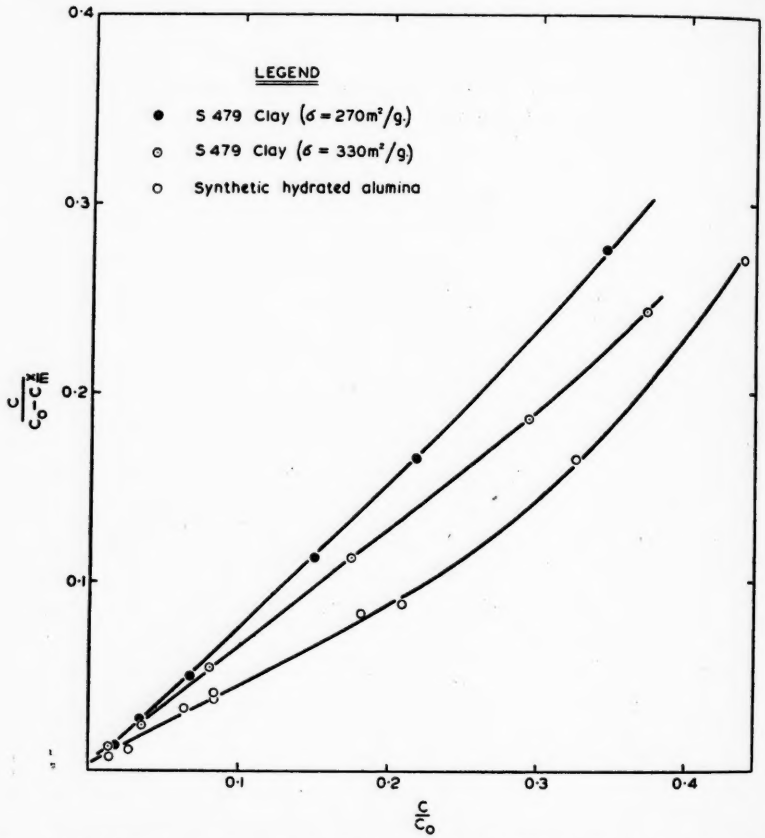

FIG. 1 (*c*) B.E.T. plot: adsorption of barium ion by NaOH-dispersed clay fractions and by hydrated alumina.

whole soils and the acid-washed clays the agreement is not quite as close, but can be considered as satisfactory (see Figs. 1 *d* and 2 *b*).

If the amounts of cation in a monolayer $(x/m)_m$ are calculated using the above equation, the results shown in Table 5 are obtained.

It can be seen that there is no simple relationship between total surface area and the amount of cation in a monolayer, such as Ewing and Liu found for their dyes. The pH range of the solutions at equilibrium

appears to have a major effect on the monolayer values found. Even if this factor of variable pH is taken into account, the specific adsorbing power in relation to surface area is quite noticeably different throughout the materials examined.

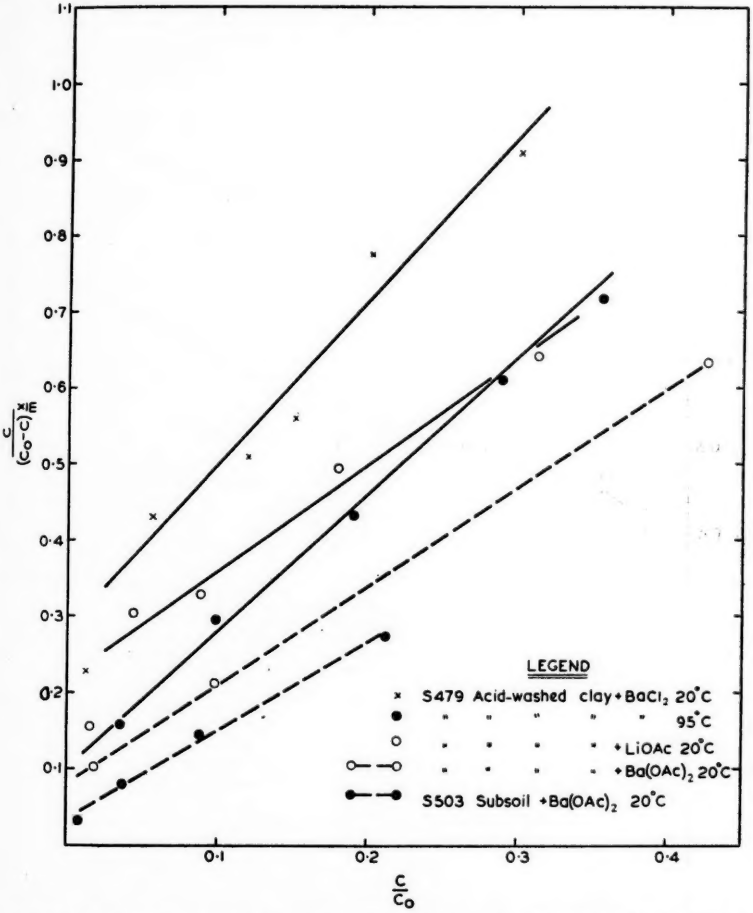

FIG. 1 (*d*) B.E.T. plot: adsorption of barium and lithium ions by soils and acid-washed clays.

The untreated soils and acid-washed clay fractions, and also the acid-washed alumina preparation, when brought to equilibrium with the acetates, gave solutions which were slightly acid. When barium chloride was used the equilibrium pH range was lower than with barium acetate, and the monolayer values were smaller. The relatively high equilibrium pH values obtained with the NaOH-dispersed clays and barium-acetate

solutions were found to be due to sodium adsorbed by the clay. Sodium amounting to 1·29 m.e. per gramme could be extracted by N/10 acetic acid from the first Whakamaru clay fraction in Table 5, and 1·54 m.e.

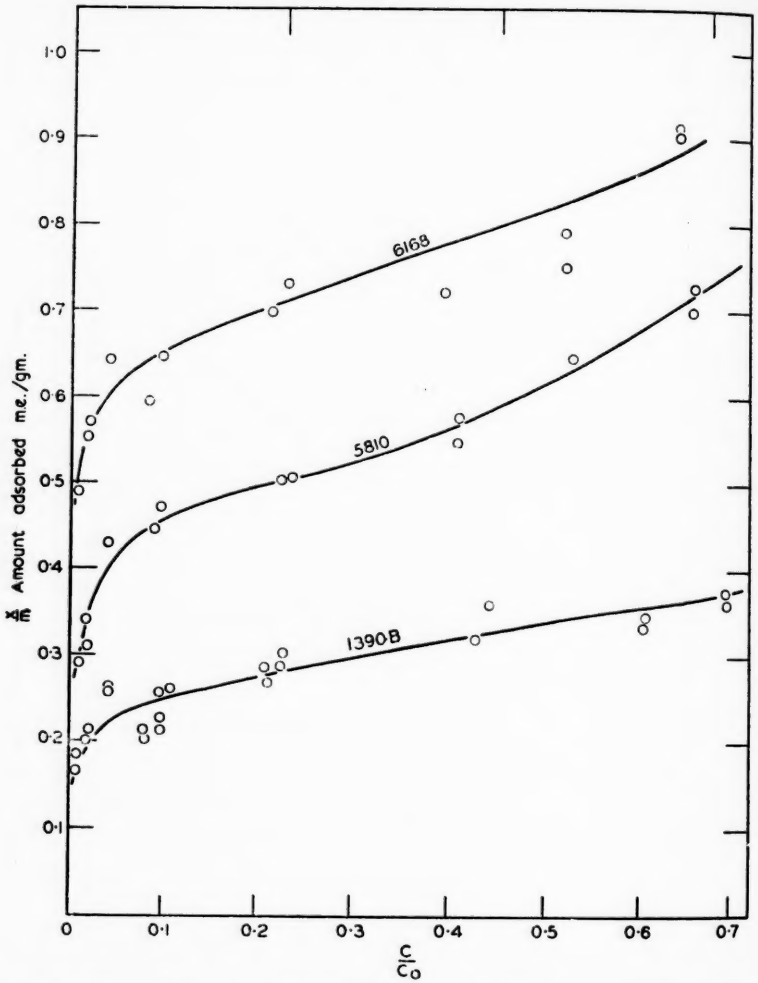

FIG. 2 (*a*) Adsorption isotherms of barium ion at 20° C. for soils containing amorphous oxides.

per gramme from the second. The extractable sodium in the alumina as prepared was 3·16 m.e. per gramme. As shown in the note under the heading in Table 6, less alkali was retained when lithium hydroxide was used for dispersing this soil.

Table 6 shows the strong effect of original pH of the salt solution on the uptake of cation, although variations on the alkaline side have apparently less effect than those on the acid side of neutrality.

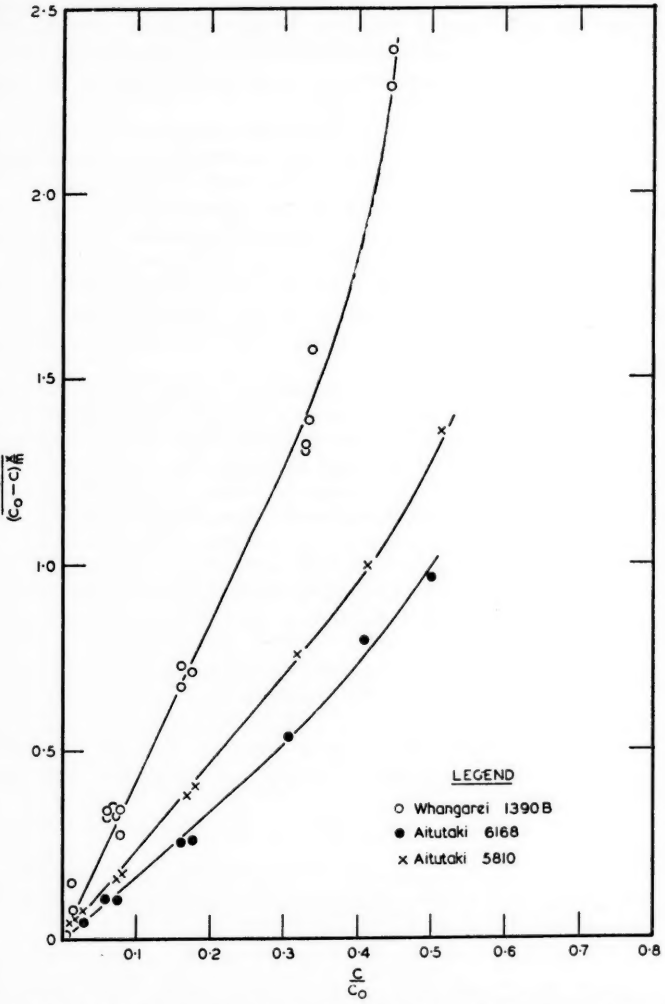

FIG. 2 (*b*) B.E.T. plot: adsorption of barium ion by soils containing amorphous oxides.

In spite of this complicating factor of pH, observations can be made from the results which lend support to the physical-adsorption theory.

1. Desorption points for the barium-chloride isotherm at 20° C. follow the adsorption curve fairly closely (Fig. 1 *b*).

2. The monolayer values for the acid-washed Whakamaru subsoil clay fraction with barium chloride at 20° C. and 95° C. are fairly close (Table 5). Owing to the rather acid reaction of the solutions at equilibrium and the presence of alumina in the solutions after heating to 95° C., it is considered that metallic salts of weak acids would have been more suitable for this comparison, but none appeared to be available which had a suitable solubility range.

3. The heat of adsorption of barium ions adsorbed from $BaCl_2$ solutions on acid-washed Whakamaru clay fraction, calculated from the B.E.T. plots in Fig. 1 *d* gave values of the order of 6,000–7,000 cals. per mole, which from published data on gas adsorption (Brunauer *et al.*, 1938) is of suitable magnitude for a physical process. The calculation was based on the procedure used by Ewing and Liu except that the heat of solution of hydrated barium chloride was obtained from the International Critical Tables, instead of being calculated from solubility data. The heat of adsorption of nitrogen (and of argon) on this sample was approximately 2,100 cals. per mole.

4. The amount of lithium in a monolayer is less than that of barium by about 20 per cent. (Table 5), even although the equilibrium pH of the barium-acetate solution is rather less than that of the lithium acetate. This result is reasonable if it is the hydrated ion which is effective in covering the available surface. Using the values given by Nachod (1949) for hydrated ionic radii, the monolayer values for Li^+ and Ba^{++} should be in the ratio 1:2·5. Shortage of the prepared clay fraction has prevented repeating the experiment with adjustment of equilibrium pH values to be approximately the same in both cases. All that can be said at present is that there is a difference in the right direction for this hypothesis to hold.

5. The monolayer values of the clay fractions of the Whakamaru and New Plymouth soils appear to be closely related to their surface areas. These clays are predominantly allophane and would be expected to produce about the same pH range in the barium-acetate solutions at equilibrium, although shortage of material prevented this being checked with the New Plymouth sample.

Other points relating to the data in Table 5 which seem worth mentioning are:

1. The 'palagonite' sample gives a rather flat isotherm suggesting that it contains also some unidentified material exhibiting the normal type of cation-exchange capacity.
2. The high cation-adsorptive capacity of the precipitated alumina might suggest that 'allophane' is an intimate physical mixture of alumina and silica in which the alumina is in a form similar to that of the preparation used in this work.
3. That the adsorption is in fact ionic is shown by the absence of any appreciable uptake of cation by Whakamaru clay fraction which had been previously dried at 105° C., from anhydrous lithium chloride dissolved in absolute methanol.

Anion Uptake

In the equilibrium experiments with barium acetate, acetate ion was found to be taken up also, but in smaller amount than barium. Similarly, chloride ion was taken up from barium-chloride solutions, but in amount considerably less than acetate (Table 7). Owing to experimental difficulties in the precise determination of acetate the scatter of plotted

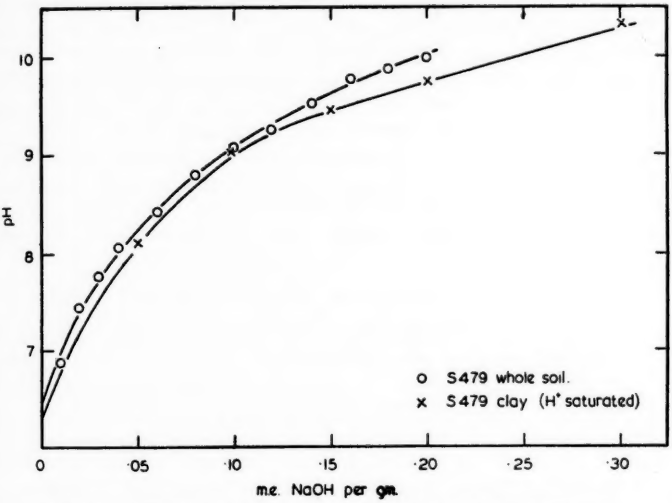

FIG. 3. Titration curves of allophane soil and clay fractions.

points is greater than for barium, but the relation between acetate taken up and residual-acetate concentration appears to be nearly linear. It can be seen that at the barium-uptake value corresponding to monolayer coverage for this clay sample (1·3 m.e. per gramme as given in Table 5) the contribution of acetate towards covering the surface will be very small, bearing in mind also that the hydrated acetate ion is generally regarded as being much smaller than the hydrated barium ion.

Titration of Allophane Clays

A clay fraction of the Whakamaru soil was prepared by dispersion of the soil with NaOH at pH 10, flocculated with NaCl after sedimentation, washed with 99 per cent. methyl alcohol, and air-dried. The clay so obtained was first washed with 100 c.c. of 0·004 N HCl, followed by 2,000 c.c. of 0·001 N HCl in 250-c.c. portions, and again washed with alcohol following essentially the procedure of Bower and Truog (1940), except for the addition of the washing with 0·004 N HCl which was found necessary with the Whakamaru soil clay fraction to ensure complete removal of sodium ion. Fig. 3 shows the titration curve for a 1 per cent. aqueous suspension of the clay so prepared. The outstanding differences in behaviour between the Whakamaru clay fraction and the

materials investigated by Bower and Truog are the much higher initial pH of the clay suspension and the lack of any inflexion point on the titration curve in the pH range shown. The titration curve of a 1 per cent. aqueous suspension of the whole soil is also shown in Fig. 3. By the standard methods of soil analysis, i.e. determining total bases and C.E.C. by leaching with N ammonium acetate, this soil would be regarded as about 27 per cent. base-saturated. It can be seen that the titration curve of the whole soil is practically identical with that of the clay fraction. In addition the amount of NaOH needed to produce a suspension of pH 10 is for both soil and clay fraction far below the cation-exchange capacity found by the leaching method, whereas Bower and Truog (loc. cit.) found that the amount of NaOH added up to the inflexion point, which was close to pH 7, corresponded to the cation-exchange capacity as usually determined. It is apparent, therefore, that both the soil and the clay fraction have relatively weak acidoid properties in spite of the apparent high saturation of the exchange complex with hydrogen both in the natural soil and in the clay fraction as prepared.

Exchangeable Hydrogen and Bases in Whakamaru Soil

The ammonium-acetate leachates from the Whakamaru soil obtained in the experiment carried out to determine the C.E.C. values given in Table 1 *b* were divided into two equal portions, and total base and exchangeable hydrogen content estimated by the usual methods. These results are given in Table 4 along with the C.E.C. values from Table 1 *b*. It will be seen that there is little change in pH of the leachate irrespective of the strength of the leaching solution. The 'exchangeable hydrogen' is fairly constant while the total base content tends to fall with decreasing concentration. The sum of bases plus hydrogen falls short of the cation-exchange capacity, the deficiency being greater the stronger the leaching solution. This may be regarded as additional evidence that the normal base-exchange mechanism is not operating.

Role of Water in the Equilibrium Tests

Whether any adsorption of water as well as of cation takes place in the equilibrium experiments cannot, of course, be determined from the results. No obvious hydration of the soil occurs except perhaps in the tests with concentrated solutions of lithium acetate, where it was more difficult to separate soil from solution after bringing to equilibrium than with barium acetate. What is striking, however, is the difference in behaviour of the allophane soils compared with bentonite, as shown in Fig. 1 *a*, considering that both materials can hold large quantities of water in the natural state, and that the B.E.T. relation is followed for uptake of cations by the amorphous minerals, although any possible movement of water in or out of the soil system is ignored.

Conclusions

Physical adsorption of cations by soils containing allophane, 'palagonite', and certain amorphous oxides is responsible to a greater or less

extent for the apparent high cation-exchange capacity shown by these soils in conventional determinations of this quantity by leaching with neutral salt solutions. Where the presence of such amorphous material is suspected in soils, the conventional C.E.C. methods should be supplemented by equilibrium experiments to test the significance of the C.E.C. values.

Acknowledgements

The authors offer their thanks to Mr. R. Q. Packard for valued assistance with the construction and operation of gas adsorption equipment, and to Dr. P. G. Harris, Dominion Laboratory, for making available a sample of 'palagonite'.

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TABLE 1

Standard Cation-exchange Capacity Determinations on Allophane Soils

(*a*) *Whenuapai soil S447A, oven-dried*

Strength of ammonium-acetate solution	*Volume used per 2-g. sample, ml.*	*C.E.C. m.e./g. (50 ml. washing alcohol)*	*C.E.C. m.e./g. (100 ml. washing alcohol)*
1·74 N . . .	50	0·427	0·363
1·74 N . . .	100	0·425	..
0·87 N . . .	100	0·399, 0·409	..
	150	0·391	..
0·438 N . . .	100	0·347	0·331
	150	0·353	..
0·087 N . . .	60	0·221	..
	110	0·221	..
	210	0·244	..
	410	0·258	..

(*b*) *Whakamaru soil S479*

Strength of ammonium-acetate solution	*Volume used per 10-g. sample, ml.*	*C.E.C. m.e./g. (100 ml. washing alcohol)*	*C.E.C. m.e./g. (275 ml. washing alcohol)*
4·26 N . . .	60	0·347	..
2·16 N . . .	60	0·340	..
2·16 N . . .	375	..	0·253
1·145 N . . .	100	0·306	..
1·145 N . . .	375	..	0·248
0·558 N . . .	200	0·239	..
0·280 N . . .	400	0·179	..
0·1175 N . . .	500	0·146	..

TABLE 2

Standard Cation-exchange Capacity Determinations on Lateritic Soils

	Strength of ammonium-acetate solution	*Volume used ml.*	*C.E.C. m.e./g.*
(*a*)	2 N	50	0·465
	1 N	50	0·435
	0·5 N	80	0·399
	0·1 N	385	0·378
(*b*)	2 N	50	0·873
	1 N	100	0·850
	0·5 N	200	0·839
(*c*)	2 N	50	0·317
	1 N	50	0·296
	0·5 N	80	0·280
	0·1 N	385	0·267

(*a*) Aitutaki Island (5810) 1·19 g. (oven-dry basis), 8×4 c.c. portions 95 per cent. EtOH.

(*b*) Aitutaki Island (6168) 0·99 g. (oven-dry basis), 8×4 c.c. portions 95 per cent. EtOH.

(*c*) Whangarei County (1390B) 1·20 g. (oven-dry basis), 8×4 c.c. portions 95 per cent. EtOH.

Soil 5810 leached first with 50 ml. 2 N ammonium acetate, followed by 100 ml. water gave a C.E.C. of 0·268 m.e. per gramme and soil 1390B with the same treatment gave a C.E.C. of 0·186 m.e. per gramme.

TABLE 3

Effect on C.E.C. Values for Whenuapai Soil S447A of Subsequent Leaching with Weaker Solutions of NH_4OAc *or Water*

Strength of original NH_4OAc *solution*	*Volume per 2-g. sample, ml.*	*Strength of second* NH_4OAc *solution*	*Volume ditto, ml.*	*C.E.C. m.e./g.*
1·74 N	100	0·87 N	100	0·378
0·438 N	100	0·087 N	400	0·257
1·74 N	22	Distilled water only	22	0·080

TABLE 4

Exchangeable Hydrogen and Bases in Whakamaru Soil S479

Strength of neutral ammonium-acetate solution	pH *of leachate*	*Standard C.E.C. from Table 1 (b), col. 3. m.e./g.*	*Exchangeable hydrogen m.e./g.*	*Total exchangeable bases m.e./g.*	*Sum of bases plus hydrogen m.e./g.*
2·16 N . .	6·83	0·340	0·075	0·067	0·142
1·145 N . .	6·80	0·306	0·062	0·084	0·146
0·558 N . .	6·78	0·239	0·057	n.d.	..
0·280 N . .	6·80	0·179	0·070	0·049	0·119
0·1175 N . .	6·55	0·146	0·068	0·044	0·112

TABLE 5

$(x/m)_m$ *Values from Equilibrium Tests*

(20° C. unless otherwise stated)

Sample	*Method of Preparation*	*Salt used in test*	*Equilibrium* pH *range*	$(x/m)_m$ *m.e./g.*	*Surface area* $m^2/g.$
S479 Whakamaru clay < 2 μ .	Dispersion of soil with NaOH, flocculation with NaCl, washed EtOH, and acetone. Dried at < 35° C.	$Ba(OAc)_2$	7·7 for N.	1·3*	270
S311 New Plymouth clay < 2 μ		,,	7·6–8·4	1·6	330
		,,	..	1·5	300
S479 Whakamaru clay < 2 μ .	As above followed by extraction with N/10 acetic acid till Na-free, then washed EtOH and acetone. Dried at < 35° C.	$Ba(OAc)_2$	6·0	0·72	330
		LiOAc	6·1–6·35	0·60	330
		$BaCl_2$	4·9–5·2	0·41	330
		$BaCl_2$, 95° C.	4·6–4·9	0·52	330
S479 Whakamaru subsoil < 2 mm.	Untreated, air-dried	$Ba(OAc)_2$	5·9–6·2	0·37	130
S503 Whenuapai subsoil < 2 mm.	,, ,,	,,	5·95–6·25	0·83	172
1390B Whangarei subsoil < 2 mm.	,, ,,	,,	6·3–6·55	0·23	75
5810 Aitutaki subsoil < 2 mm. .	,, ,,	,,	6·6–6·7	0·425	94
6168 Aitutaki subsoil < 2 mm. .	,, ,,	,,	6·3–6·6	0·59	102
Hydrated alumina	Ppn. by CO_2 from sodium aluminate[3]	$Ba(OAc)_2$	7·7	2·33	180
,, ,,	As above followed by extraction with N/10 acetic acid till Na-free, then washed EtOH and acetone. Dried at < 35° C.	,,	6·6	1·02	180
'Palagonite' .	Separated from Aitutaki subsoil 6168 (ref. 4/7)	$BaCl_2$	4·2–4·8	0·435	86

* A monolayer value of 0·72 m.e. per gramme would be required to give uniform surface coverage of this clay fraction by the hydrated barium ion.

TABLE 6

Effect of Initial pH *on Barium Uptake for Whakamaru Clay Fraction*

(1 g. of clay separated by dispersion of soil with LiOH and containing 0·69 m.e. Li, brought to equilibrium with 10 ml. approx. N barium acetate in each case)

Original pH	*Final* pH	*Amount of* Ba *adsorbed* m.e./g.
4·3	4·4	0·606
6·0	6·1	0·988
7·0	7·3	1·372
11·1	7·45	1·395

TABLE 7

Anion Adsorptions at 20° C.

(*a*) *Acetate: S479 clay* (NaOH *dispersed*) *and* $Ba(OAc)_2$ *at* pH 7·0

Original strength	*Barium uptake m.e./g.*	*Acetate uptake m.e./g.*
3·166 N . . .	2·30	1·31
2·477 N . . .	2·07	0·92
2·018 N . . .	1·91	0·78
1·072 N . . .	1·70	0·43
0·485 N . . .	1·47	0·29
0·096 N . . .	1·28	0·16

(*b*) *Chloride: S479 clay* (NaOH *dispersed*) *and* $BaCl_2$ *at* pH 7·0

Original strength	*Barium uptake m.e./g.*	*Chloride uptake m.e./g.*
1·995 . . .	n.d.	0·068
1·00 . . .	1·202	0·02
0·50 . . .	1·103	0·002
0·253 . . .	1·085	nil
0·065 . . .	0·942	nil

VARIATIONS IN THE UPTAKE BY PLANTS OF SOIL PHOSPHATE AS INFLUENCED BY SODIUM NITRATE AND CALCIUM NITRATE

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Introduction

IN former publications the influence of neutral salts on the solubility of soil phosphate (Lehr and van Wesemael, 1952; van Wesemael and Lehr, 1954) has been dealt with. It has been shown that in general neutral salts reduce the solubility, but that the measure of this effect is largely determined by the cation. In the case of salts with the same anion the reducing effect on the solubility of soil phosphate increases in the order of the lyotropic series $Na < K < Mg < Ca$.

In the investigation described here the authors undertook to show that the changes in phosphate solubility induced by fertilization do, in fact, give rise to differences in the absorbability of soil phosphate by the plant. The experiments were based on the Neubauer method (Neubauer and Scheider, 1923) which in its original form is designed to determine, by the use of seedlings, the amount of available soil phosphate and other plant nutrients. In the usual method for Neubauer experiments no nitrogen, phosphate, or potassium is added. For the present purpose, however, nitrogen was added in order to compare the phosphate uptake when fertilizing with sodium nitrate and calcium nitrate.

Before the main investigation was commenced a series of exploratory experiments was carried out for general guidance purposes. These were based upon the method described in *Diagnostic Technics* (American Potash Institute, 1948, pp. 211, 212), tested and modified to suit the purpose. The experience thus gained showed that:

(*a*) Summer wheat was more suitable than rye for the investigation owing to its greater sturdiness and more regular germination.

(*b*) To obtain sturdier plants the number of plants per culture dish should be reduced from 100 to 50.

(*c*) The nitrogen dose must be greater (relative to volume of soil) than is usual in pot experiments.

(*d*) To prevent damage to the seed through too strong salt concentrations it is desirable to allow the seed to germinate before applying nitrogen, and to obtain more regular development of the plants it is better to divide the total nitrogen dose into smaller doses given at intervals.

(*e*) By using as basis 250 g. of soil in place of 100 g., higher uptake values and better defined reactions are obtained. In subsequent experiments, therefore, 250 g. of soil was always used.

The uptake of sodium by both wheat and rye is relatively small. Although the possibility of physiological influence of sodium on

phosphate uptake is not entirely excluded, it need not seriously be taken into account.

Experiments with Increasing Doses of Nitrogen

In 1952 experiments were commenced using increasing nitrogen doses on three different types of soil, viz.:

	pH	P-*water* (50° C.) *mg.* P_2O_5 *per* 100 *g.*	P-*water* (20° C.) *p.p.m.*	P-*citric* *mg.* P_2O_5 *per* 100 *g.*	% *humus*
1. Poor loamy soil	4·7	1·2	6·3	35	2·4
2. Reclaimed sandy heath soil	5·0	0·5	2·2	14	6·7
3. Old agricultural land (humic sand)	5·9	1·2	5·2	30	3·4

Here, and in the following, P-water refers to water-soluble P_2O_5 determined in a 1:5 soil-water mixture after allowing to stand for 24 hours at 50° C. P-citric refers to P_2O_5 soluble in 1 per cent. citric acid at room temperature, with a 1:5 soil-solution ratio.

With the first two soils no important difference in phosphate uptake resulting from the two nitrate fertilizers was observed, due in the loamy soil to its low pH and in the reclaimed heath soil to the low percentage of phosphate (compare also Fig. 3).

The experiment with soil 3 contained three nitrogen levels, viz. 56, 112, and 280 mg. N respectively, in the form of sodium nitrate and calcium nitrate. These amounts were given in four equal parts at intervals of between 5 and 8 days.

In addition separate series were made:

(*a*) without phosphate, and
(*b*) with 50 mg. $CaHPO_4.2H_2O$ mixed with the soil.

The experiments were carried out in triplicate and took a month to complete.

The dry-matter weights of root and above-ground parts of the plants in each of the dishes were measured separately as were also the phosphate percentage and the total-phosphate content.

TABLE 1

Results of Series A (without Phosphate)

(*Average of 3 dishes*)

Nitrogen fertilizer	*Above-ground parts*			*Roots*			*Whole plant*
	g. dry-matter	% P_2O_5	*mg.* P_2O_5	*g. dry-matter*	% P_2O_5	*mg.* P_2O_5	*mg.* P_2O_5
$Ca(NO_3)_2$ 0·05 N	4·02	0·49	19·7	1·84	0·36	6·6	26·3
0·10 N	4·42	0·46	20·3	1·86	0·34	6·3	26·6
0·25 N	4·35	0·38	16·5	1·61	0·34	5·5	22·0
$NaNO_3$ 0·05 N	4·25	0·60	25·5	1·89	0·35	6·6	32·1
0·10 N	4·17	0·55	22·9	1·76	0·38	6·7	29·6
0·25 N	4·17	0·48	20·0	1·47	0·33[5]	4·9	24·9
No N	2·90	0·81	23·5	1·38	0·39	5·4	28·9

TABLE 2

Results of Series B (with Phosphate)

(*Average of 3 dishes*)

Nitrogen fertilizer	Above-ground parts			Roots			Whole plant
	g. dry-matter	% P_2O_5	mg. P_2O_5	g. dry-matter	% P_2O_5	mg. P_2O_5	mg. P_2O_5
$Ca(NO_3)_2$ 0·05 N	4·15	0·64	26·6	1·96	0·38[5]	7·6	34·2
0·10 N	4·68	0·53	24·8	1·79	0·37[5]	6·7	31·5
0·25 N	5·08	0·46	23·4	1·55	0·35	5·4	28·8
$NaNO_3$ 0·05 N	3·38	0·74	28·3	1·60	0·42	6·7	35·0
0·10 N	4·28	0·63	27·0	1·77	0·45[5]	8·1	35·1
0·25 N	3·97	0·61	24·2	1·76	0·47	8·3	32·5
No N	3·12	0·95	29·6	1·75	0·43	7·5	37·1

In a blank experiment (with glass sand instead of soil) the plants were found to contain a total of 23·3 mg. P_2O_5: which compared very closely with the phosphate contained in 50 seeds (23·4 mg. P_2O_5). For the plants without nitrate fertilization in series A (no additional phosphate), the total uptake was therefore 5·5 mg. P_2O_5, and in series B (with phosphate) 13·7 mg. P_2O_5. The effects of the amounts and forms of the nitrate fertilizer may best be seen from Fig. 1.

The recession of the phosphate percentages as the nitrate concentrations are increased may chiefly be ascribed to the restraining of the phosphate solubility (Lehr and van Wesemael, 1952). In the recession of the total contents, the slight decline in yields has also played a part.

In comparison with the phosphate originally contained in the seeds the uptake of phosphate from the culture medium is relatively small but it has, nevertheless, clearly been influenced by the calcium and sodium introduced by nitrate fertilization. This influence is to be seen most clearly in series A, where the plants had to rely upon the phosphate present in the soil. In series B, where a greater amount of phosphate was available, the effect of the cations on the uptake of phosphate was smaller.

Experiments with Various Soils

In 1953 and 1954 an investigation was carried out in which twenty-two humic sandy soils, of various origin and phosphate content, and one loamy soil were compared with each other with regard to the effect of calcium and sodium ions on uptake of phosphate.

The investigation was limited to a comparison of $Ca(NO_3)_2$ and $NaNO_3$ when applying a single dose of nitrogen amounting to 112 mg. per dish. In order to simplify the technique, only the above-ground parts of the plants were sampled, as it is in these parts that most of the phosphate is recovered and the percentage values of the roots do not, in any case, differ very considerably. In neither year was additional phosphate added in the experiments so that the uptake was related solely to the soil phosphate of the various soils.

The plant development of the two series in 1953 and 1954 was not entirely comparable, due not only to weather conditions but also to seed variations. In order to give an impression of the differences in

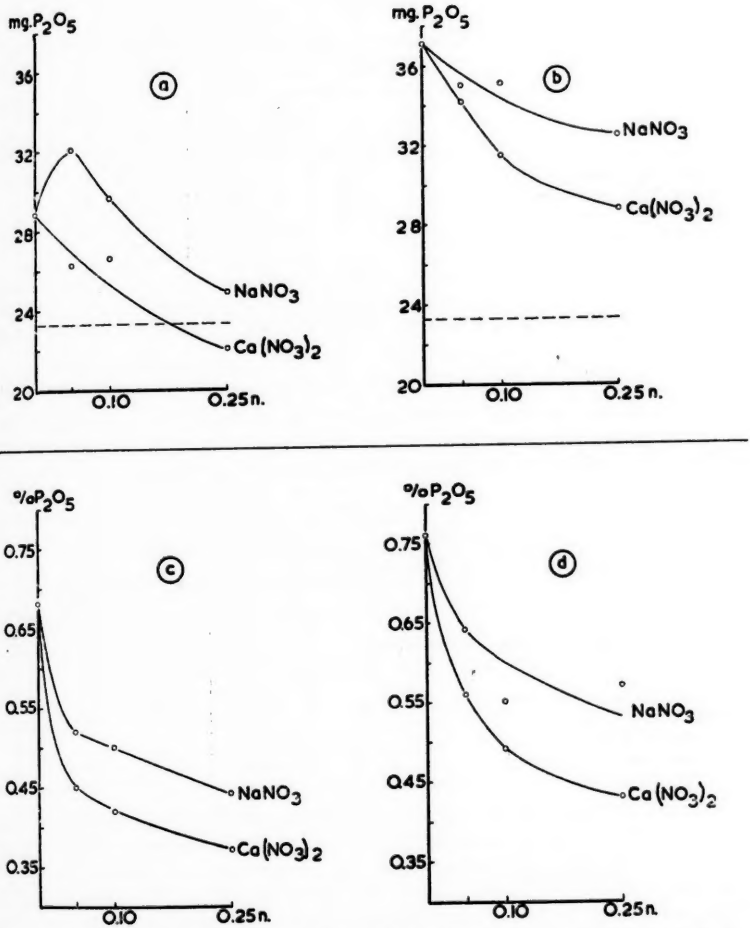

FIG. 1. (*a*) Phosphate content of wheat plantlets in relation to strength of nitrate solution added in series A (without phosphate). (*b*) Phosphate content of wheat plantlets in relation to strength of nitrate solution added in series B (with phosphate). (*c*) Phosphate percentage of wheat plantlets in relation to strength of nitrate solution added in series A (without phosphate). (*d*) Phosphate percentage of wheat plantlets in relation to strength of nitrate solution added in series B (with phosphate).

development, the following tables summarize the mean results obtained during these years.

TABLE 3

Average Results of Neubauer Experiments in Various Soils in 1953 and 1954

	1953		1954	
	$NaNO_3$	$Ca(NO_3)_2$	$NaNO_3$	$Ca(NO_3)_2$
Average dry-matter yield (g.)	2·79	2·96	2·24	2·39
Average P_2O_5 percentage	0·58	0·48	0·68	0·53
Average P_2O_5 content (mg.)*	15·78	13·86	15·45	13·14
Extractable water-soluble soil P_2O_5 (p.p.m.) at room temperature	6·5	3·9	8·0	5·0

* To calculate the amounts of P_2O_5 which were actually absorbed from the soil a correction must be made, which for 1953 is 9·8 mg. P_2O_5 and for 1954 is 7·3 mg. P_2O_5.

With regard to the matter under investigation almost identical results were obtained in both years despite the difference in development. These results are reviewed to the best advantage by expressing the results for $NaNO_3$ as percentages of those for $Ca(NO_3)_2$.

TABLE 4

Neubauer Experiments in Various Soils

Results for $NaNO_3$ *expressed in Percentages of* $Ca(NO_3)_2$

Average results for above-ground parts	*1953*	*1954*	*Average 1953–4*
Dry-matter yield	94	93·5	94
P_2O_5 percentage of plant	120	128	124
Total P_2O_5 present	114	118	116
P_2O_5 uptake from soil	150	140	145
Water-soluble P_2O_5 in soil	167	150	158·5

On the average the phosphate solubility with $NaNO_3$ fertilization was 64 per cent. greater than with $Ca(NO_3)_2$ fertilization. The average phosphate uptake (calculated from the phosphate present in the above-ground parts of the plant) was 45 per cent. greater in the case of $NaNO_3$ than with $Ca(NO_3)_2$. The influence of the two cations upon the phosphate uptake is therefore unmistakable.

Fig. 2 A shows the phosphate uptake of the separate soils dependent upon the water-soluble P_2O_5 (in mg. per 1,000 g. at room temperature). In Fig. 2 B it is shown how the phosphate solubility in the soil varies due to the addition of $NaNO_3$ and $Ca(NO_3)_2$.[1] The trend of this relation is almost linear and the difference in solubility continues to increase for both nitrate fertilizers and therefore also for larger phosphate values in

[1] In this determination 250 g. soil was treated with 40 c.c. 0·1 N $NaNO_3$ and $Ca(NO_3)_2$ respectively, air-dried, and the soluble phosphate estimated by extraction at room temperature.

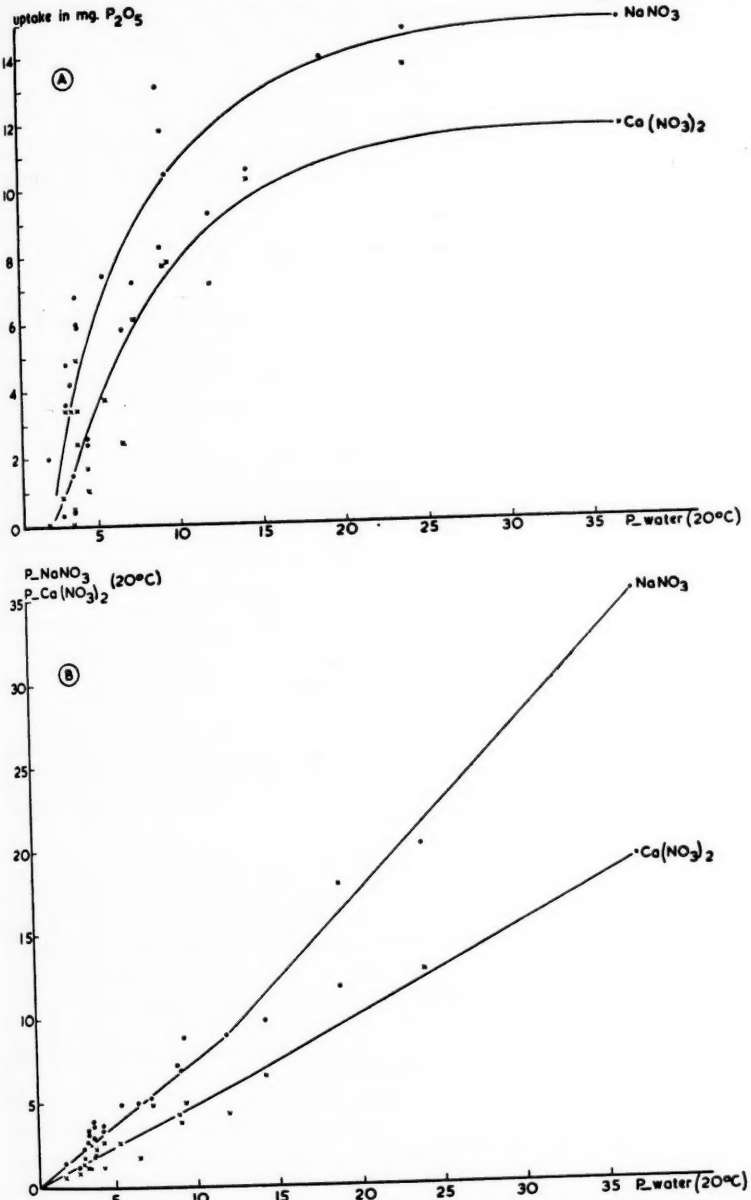

FIG. 2. (A) Uptake of phosphate by wheat plantlets dependent upon phosphate level of the soil (expressed as water-soluble P_2O_5 at 20° C.). (B) Relation between the solubility in water of soil phosphate with and without dressing with $NaNO_3$ and $Ca(NO_3)_2$, respectively.

the soil. As against this, however, the uptake of phosphate by the plant at higher phosphate levels in the soil approaches a limit resulting in both curves running roughly parallel.

In order to explain the deviations of individual points in Fig. 2 A relationships with other soil factors were investigated. An indication of such a relationship was established only in respect of the pH. Although uptake, as such, shows only a slight dependence on the pH of the soil

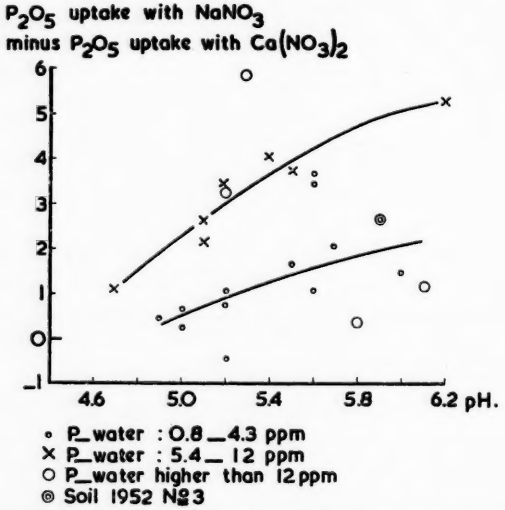

FIG. 3. Difference in phosphate-uptake when dressing with $NaNO_3$ and $Ca(NO_3)_2$, of wheat plantlets in different soils, arranged according to: (*a*) low, medium, and higher phosphate levels in the soil; (*b*) ascending pH-values. The results at low and medium phosphate levels suggest an influence on the phosphate uptake by both pH and phosphate level.

a more regular connexion was found in the difference in phosphate uptake from $NaNO_3$ and $Ca(NO_3)_2$ by the plants. This is to be seen in Fig. 3 in which all difference values are summarized under groups for soil with lower and soils with higher quantities of available phosphate, and plotted against the pH. The figure thus obtained suggests, apart from dependence upon the phosphate level, a connexion with the pH value of the soil. It should also be noted that the values for soils with a high phosphate availability (above 12 p.p.m. water-soluble P_2O_5) cannot be fitted into the general trend of the figure.

With regard to the practical meaning of the effect described above it is obvious that it is only of consideration in soils with low phosphate contents. It may be seen from Fig. 2 A that especially in the range of low P values, the phosphate uptake is favourably influenced by sodium. This is expressed in figures in Table 5 by calculating the ratio of phosphate uptake with $NaNO_3$ and $Ca(NO_3)_2$, for soils with increasing phosphate availability.

TABLE 5

Dependence of the Effect of $NaNO_3$ *and* $Ca(NO_3)_2$ *on Phosphate Uptake with Ascending Phosphate Levels in the Soil*

Soil-phosphate P-*water* (*p.p.m.*) 20° *C.*		*Mean uptake in mg.* P_2O_5 *per culture dish*		*Ratio of uptake values*
Range	*Mean*	*With* $NaNO_3$	*With* $Ca(NO_3)_2$	$NaNO_3/Ca(NO_3)_2$
1·8– 3·4	2·9	2·4	1·6[5]	1·46
3·7– 4·3	3·9	4·7	2·7	1·74
5·4– 7·2	6·4	6·8	4·1	1·66
8·9–11·9	9·8	11·1	7·7	1·44
14·0–37·0	..	13·4	10·8	1·24

The ratio values shown here should not be taken as absolute as they are dependent on the correction applied. Nevertheless the decreasing trend with increasing soil phosphate is sufficiently illustrated.

Summary

As a sequel to laboratory experiments carried out to determine the effects of various cations upon the solubility of soil phosphate, a series of Neubauer experiments was made to ascertain whether the results established in the laboratory experiments also held good for the uptake of phosphate by the plant. By fertilizing summer wheat with sodium nitrate a substantial increase in phosphate uptake could indeed be established, as compared with the uptake when fertilizing with calcium nitrate. Averaged over a series of experiments with twenty-two humic sandy soils it was found that 45 per cent. more phosphate was absorbed from the soil when fertilizing with sodium nitrate than when fertilizing with calcium nitrate. This effect was also observed when the phosphate level of the soil was low, which in practice entails the risk of a resultant phosphate deficiency.

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THE ORGANIC-MATTER AND NITROGEN STATUS OF EAST AFRICAN SOILS

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RECENT work by Jenny and co-workers (1948, 1949) on soils from Colombia and Central America proves conclusively that the nitrogen-temperature relationships found by Jenny (1930) for North American soils do not apply to the tropics. Extrapolation of the nitrogen-temperature curves to the high annual temperatures prevailing in the tropics had led Jenny to expect that tropical soils would be very low in nitrogen and organic matter. In actual fact, from localities with identical mean annual temperatures and rainfall, the nitrogen and organic-matter levels of Colombian soils proved to be severalfold higher than those of United States soils. Similarly, Smith *et al.* (1951) found that soil organic matter and nitrogen reserves are relatively high in Puerto Rico over a wide range of rainfall. They believe that the relatively strong resistance of deep Puerto Rican soils to deterioration is a natural consequence of the rather high organic-matter contents extending to considerable depth. They conclude that high clay contents, predominance of kaolinite as the clay mineral, and relatively deep well-drained tropical soil profiles are compatible with high organic-matter and nitrogen levels, but that the predominant factor in the organic-matter balance is climatic and biotic.

During the routine analysis of East African soils, a considerable amount of data has accumulated, including their organic-matter, nitrogen, exchangeable-base, sand, silt, and clay contents, pH and base-exchange capacities. Altogether 420 surface soils (0–6 in.) from fertilizer trials and 138 profile samples from the Soil Survey Division have been analysed. The profile samples were of particular interest since they were collected from sea-level to 10,000 ft., and therefore covered a wide range of climatic conditions and soil types, data for most of which were available. For example, rainfall conditions ranged from 17 to 71 in. per year and average temperatures from 54° to 80° F. (12–27° C.). This provided an excellent opportunity for determining the extent to which the amounts of organic matter in East African soils, and the factors governing this, conform to those already found for other tropical countries, since both major factors (climate) and minor factors (soil type, clay content) could be taken into consideration. Additional interest attaches to the results because, so far, little has been published on the overall organic-matter status of East African soils.

Materials and Methods

Organic-matter determinations were made by the Walkley-Black (1934) method on soil samples which had passed through a 40-mesh sieve. The percentage carbon (uncorrected) was multiplied by two to

obtain the percentage of organic matter, which is expressed on an air-dry basis. Total nitrogen was determined by Kjeldahl's method.

In selecting the data for analysis, attention was confined almost entirely to the profile samples for the following reasons: (*a*) the bulk of the samples were from open uncultivated sites, thereby minimizing the effect of cultural practices on the organic-matter content; (*b*) for each profile the organic-matter contents could be calculated for 0–1 ft., thus putting them on a comparable basis; (*c*) the samples covered a wide range of climate and known soil types.

In attempting to relate the organic-matter status of the soils to various factors, account had to be taken of the major factors having an overall influence, and minor factors having a modifying influence. Major factors according to Jenny *et al.* (1948) and Smith *et al.* (1951) appear to be elevation, climate, and biotic conditions, while minor factors include amount and kind of clay, and depth and development of the profile (Smith *et al.*, 1951). It is, however, difficult to disentangle the effects of the various factors in East Africa, since they are interrelated to the extent that both rainfall and temperature are partly functions of altitude. The problem is further complicated by the influence of minor factors such as soil type and drainage. In presenting the data, therefore, the amounts of organic matter are related separately to altitude and rainfall, which proved to be the major factors governing the organic-matter content of East African soils. Minor factors, e.g. temperature, soil type, amount and kind of clay, are discussed as and when they influence the organic-matter content under standard altitude and rainfall (major factor) conditions.

The following sections deal first with the organic-matter contents of all the surface soils. The relationships between organic matter and climate and the influence of minor factors for the surface profile samples are then presented. This is followed by a general discussion of the results found for the East African soils.

The Organic-Matter Content of the Surface Soils

This is summarized in Fig. 1, based on 570 surface samples from fertilizer trials and soil survey profiles. They are not corrected to a standard depth but the bulk of them are 0–6 in. samples. In view of the large number of samples involved and the wide area over which they were collected, it gives a fair indication of the range of organic-matter contents met with in East African soils.

An interesting feature is the large proportion of the soils (47 per cent.) that contain over 4 per cent. organic matter. Many of these soils are from the Kenya Highlands and have been under cultivation for anything up to 35 years. In spite of this the organic-matter contents are still fairly high (about 5–8 per cent.) except for a particular group of shallow soils whose organic-matter contents range from about 2·5 to 4·0 per cent. and where continuous wheat cultivation and burning of the crop residues has been practised. Contributory factors to the high organic-matter status are no doubt the altitude (5,000–8,000 ft.) and rainfall (40–60 in.) of

the Highlands. Equations (1) and (5) show that such conditions favour relatively high organic-matter contents in the soil.

Organic-matter values below 2 per cent. are generally referable to sandy soils, and soils under low rainfall, while high values, particularly those over 6 per cent., are generally associated with high rainfall and/or soils at high altitudes. These relationships are discussed more fully later.

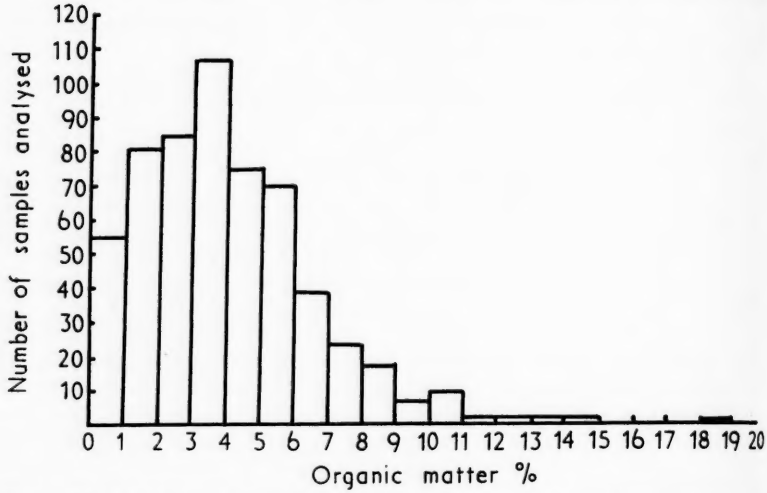

FIG. 1. Number of surface samples analysed and the ranges of organic-matter contents into which they fall.

For purposes of comparison, Bonnet (1941) in Puerto Rico found an average of 3·54 per cent. for the humid areas and 1·84 per cent. for the arid areas. For some typical soils of the United States, Smith *et al.* (1951) report a range of organic matter from 22 to 76 tons per acre ft. of soil, assuming that 12 in. of soil per acre weighs 3,500,000 lb. The average organic-matter content of the surface 12 in. of the 138 profile samples in East Africa was 3·36 per cent. This corresponds to 53 tons per acre ft., a figure in excess of any of the six typical United States soils quoted by Smith *et al.* (1951) apart from the Caribou loam which contained 76 tons per acre. Dean (1930) reported a mean organic-matter content of $3{\cdot}75 \pm 0{\cdot}03$ per cent., and a mean nitrogen content of $0{\cdot}31 \pm 0{\cdot}004$ per cent. for 223 Hawaiian soils, referring mainly to the surface 12 in. For the East African profile samples the mean values for 138 samples (surface 12 in.) were $3{\cdot}33 \pm 0{\cdot}16$ per cent. organic matter and $0{\cdot}19 \pm 0{\cdot}009$ per cent. nitrogen.

The Relationship between Organic Matter and Altitude

When the organic-matter contents of the surface soils (0–12 in.) from the 138 profiles was plotted against altitude, the scatter diagram (Fig. 2) showed a significant trend of increasing organic matter with altitude.

This was to be expected since increasing altitude is associated here with increasing rainfall (see later) and decreasing temperature. According to Jenny (1941) increasing rainfall favours greater plant growth without having much effect on the rate of decomposition, while decreasing temperature slows down the decomposition processes more rapidly than the growth of the plant. The regression of percentage organic matter (O.M.)

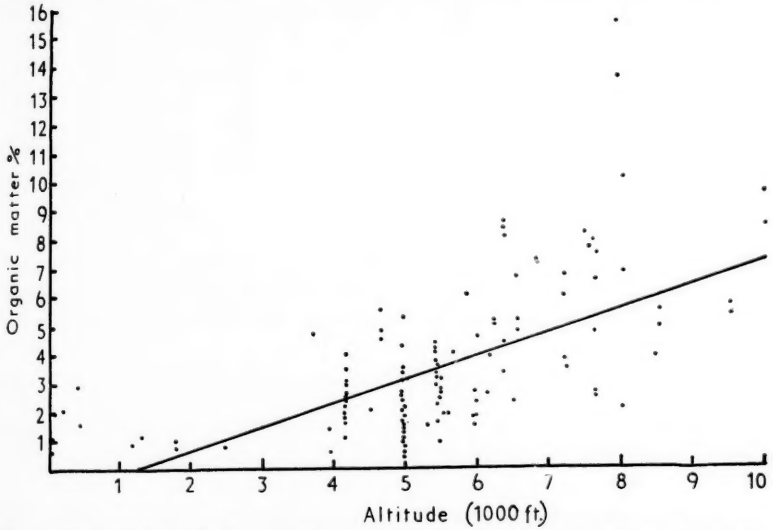

FIG. 2. The relationship between the percentage organic matter in the surface soils (0–12 in.) and altitude.

on altitude (equation (1)) is very significant and indicates that on an average each 1,000 ft. increase in altitude in East Africa is associated with a 0·8 per cent. increase in organic matter.

$$\%\ \text{O.M.} = 0{\cdot}0008\ \text{alt.} - 0{\cdot}9\ (t = 9{\cdot}31,\ \text{for P} = 0{\cdot}001,\ t = 3{\cdot}291) \quad (1)$$

The relationship has been expressed in its simplest form as a straight regression because there was no evidence that the critical altitude had been reached above which the organic-matter content then starts to decline. This critical altitude lies in East Africa above 10,000 ft., as shown in Table 1, which refers to samples collected on the slopes of Kilimanjaro and the Ruwenzori range.

At certain altitudes there is a considerable amount of scatter about the regression line. This, in many instances, is due to differences in climatic and soil conditions. Thus at 4,200 ft. the four highest organic-matter values are associated with high rainfall (55–60 in.), and the remaining values with low rainfall (about 25 in.). Three relatively high organic-matter contents at 4,600 ft. are also associated with high rainfall (52 in.). The wide range of organic-matter contents at 5,000 ft. is related both to rainfall and clay content. The two highest values are associated

TABLE 1

The Organic-matter Contents of Some High Altitude Soils

Altitude (feet)	*Depth (inches)*	*% O.M.*	*% N*	*C/N*	*Remarks*
9,000	0–6	38·2	1·64	15·5	Evergreen forest
	6–18	18·4	0·56	21·9	Evergreen forest
9,000	0–4	33·8	1·10	20·4	Moorland
	4–8	20·8	0·71	19·5	Moorland
	8–15	14·4	0·38	25·2	Moorland
12,000	0–4	7·0	0·18	25·9	Moorland
	4+	1·2	0·05	16·0	Moorland
12,500	0–4	10·8	0·28	25·7	Moorland
	4+	6·4	0·17	25·0	Moorland
12,000	0–12	12·4	..	..	Old moraine
14,600	surface	3·4	..	..	Foot of glacier

with a 36 in. rainfall, and the rest with a 25 in. rainfall. In this low rainfall group the percentage organic matter was found to be very significantly and directly related to the percentage clay in the soil (equation (2), 27 observations).

$$\% \text{ O.M.} = 0{\cdot}029\% \text{ clay} + 0{\cdot}88 \; (t = 3{\cdot}09, \text{ for } P = 0{\cdot}01, \; t = 2{\cdot}787) \quad (2)$$

A similar relationship was found for the soils at an elevation of 5,400 ft., the rainfall ranging from 35 to 38 in. (equation (3), 15 observations).

$$\% \text{ O.M.} = 0{\cdot}039\% \text{ clay} + 0{\cdot}97 \; (t = 3{\cdot}72, \text{ for } P = 0{\cdot}01, \; t = 3{\cdot}012) \quad (3)$$

It appears from equations (2) and (3) that under constant altitude and rainfall conditions the percentage clay in the soil can influence the organic-matter content roughly to the extent that a 10 per cent. increase in clay content causes a 0·3 per cent. increase in the percentage organic matter. Smith *et al.* (1951) consider the kind and amount of clay to be a minor factor influencing organic-matter content and the regression coefficients of equations (2) and (3) confirm this.

The three outstandingly high values at 6,400 ft. refer to soils which are about 98 per cent. base unsaturated, conditions repressing microbiological activity and favouring organic-matter accumulation. The very high organic-matter contents at 7,900 ft. refer to forest soils under high rainfall, and the slightly low values at 8,250 ft. to a rather unusual shallow siliceous soil underlain by a heavy montmorillonitic clay on which run-off occurs during heavy rains. As a further example of the effect of soil type on organic-matter content, mention may be made of a number of profiles not included in Fig. 2, from an area over which there was little variation in altitude (3,800 ft.) or rainfall (45 in.). Here the organic-matter content of the sandy soils (0–12 in.) averages about 1·5 per cent. while that of the heavy bottom-land soil averages about 4 per cent.

Equation (4) shows the altitude-nitrogen relationship (the % N

referring to that in the surface foot of soil) which was, like equation (1), very significant ($P < 0.001$).

$$\% N = 0.00004 \text{ alt.} - 0.0456 \quad (4)$$

Altitude itself, however, cannot be considered as a factor directly governing the organic-matter and nitrogen contents of soils. Since rainfall was found to be very significantly and directly related to altitude

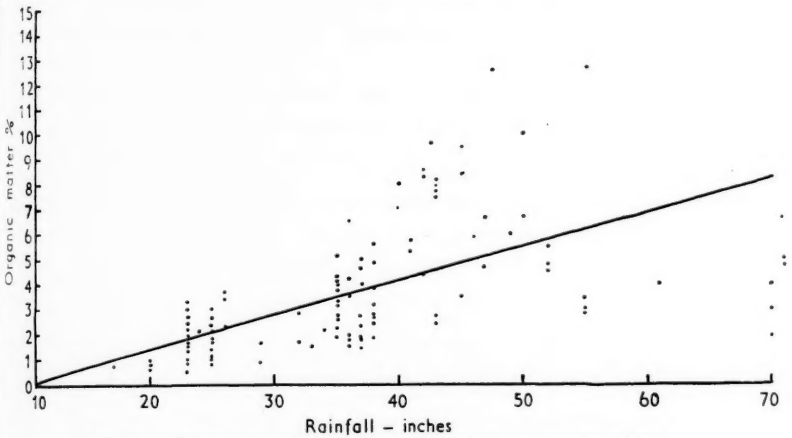

FIG. 3. The relationship between organic matter and rainfall.

($P < 0.001$) and in view of what is said later about the relative effects of temperature and rainfall on the organic-matter contents of the soils it is apparent that the relationships expressed by equations (1) and (4) are largely a function of rainfall.

The Relationship between Organic Matter and Rainfall

In relating organic-matter content to rainfall, average annual rainfall values were taken, and no allowance was made for rainfall distribution. The regression of the percentage organic matter on rainfall was very significant (equation (5)), but slightly less so than that of organic matter on altitude, possibly because altitude is an integration of rainfall and temperature.

$$\% \text{ O.M.} = 0.131 \text{ in. rain} - 1.21 \ (t = 8.95, \text{ for } P = 0.001, t = 3.291) \quad (5)$$

In deriving this equation two soils were omitted. Although under high rainfall, 65 and 58 in., they contained only 0·7 and 1·1 per cent. organic matter respectively. The first of these, however, contained 88 per cent. sand, the other 81 per cent. This would severely restrict the effect of rainfall on plant growth, and therefore on organic-matter accumulation. In arriving at a general relationship between organic matter and rainfall their omission was considered justified. With this slight modification the scatter diagram of organic matter on rainfall (Fig. 3) was similar to that

on altitude and again showed, in this scatter, the modifying effect of minor factors on the major (rainfall) factor.

From equation (5) each 10 in. increase in rainfall is associated with an increase of 1·3 per cent. organic matter in the soil, and no organic matter is to be expected when the annual rainfall is less than 9 in. Actually, in the northern parts of Kenya where such rainfall does occur the soils contain from 0·5 to 1·0 per cent. organic matter, due largely to rainfall distribution. The rains fall over a relatively short period, permitting rapid seasonal growth followed by a long period of dormancy.

When percentage nitrogen in the soil (0–12 in.) is related to rainfall, equation (6) is obtained.

$$\% \text{ N} = 0{\cdot}00665 \text{ in. rain} - 0{\cdot}061 \quad (P < 0{\cdot}001) \tag{6}$$

This may be compared with equation (7) derived by Jenny and Leonard (1934) for soils (0–10 in.) of the loess belt in the Middle West along the annual isotherm of 51·8° F. (11° C.); and with equation (8) derived from data published by Russell and McRuer (1927) for Nebraskan silt loam soils (0–12 in.).

$$\% \text{ N} = 0{\cdot}00655 \text{ in. rain} - 0{\cdot}023 \tag{7}$$

$$\% \text{ N} = 0{\cdot}00740 \text{ in. rain} + 0{\cdot}001 \tag{8}$$

From the similarity of equations (6), (7), and (8) it appears that the effect of rainfall on the nitrogen content of the soil is roughly the same under the conditions described for America and East Africa. Equations (7) and (8), however, each refer to a particular soil type under more or less constant temperature conditions, while equation (6) refers to a number of soil types under a temperature range of 54–80° F. In this connexion, however, Prescott (1931) found no direct effect of temperature on the nitrogen content of Australian soils over a range of 56–77° F., and for a similar temperature range none was found in these studies (see following section). On this basis, and assuming that soil type is a minor factor, compared with rainfall, in governing soil nitrogen content, comparison of equation (6) with equations (7) and (8) becomes more valid. It appears that the influence of rainfall on soil nitrogen is similar, under the conditions described, for East Africa and North America in spite of big seasonal temperature differences. To the extent, however, that temperature affects both the synthesis and breakdown of organic matter and nitrogen these temperature differences may be relatively unimportant. Thus while microbiological activity with concomitant loss of organic matter and nitrogen is less in temperate than tropical climates the production of organic matter and nitrogen is also less, particularly where frost occurs. This effect of temperature on two opposite processes, synthesis and breakdown, helps to explain why the nitrogen/rainfall relationships can be so similar in spite of such divergent temperatures. Another example of such similarity is the relationship between total nitrogen content and the humidity factor as reported by Jenny (1930) for North America, and Prescott (1931) for Australia. For a given humidity factor the nitrogen contents for the two countries are approximately the same.

The Relationship between Organic Matter and Temperature

Since decreasing temperature was often associated with increasing rainfall the effect of temperature alone on soil organic matter could only be determined by selecting as far as possible groups of soils under fairly constant rainfall but covering a range of temperature. Two groups of soils (1 and 2) were thus selected and, for contrast, a third group (3) in which temperature was constant and rainfall varied.

Group 1. Rainfall (40–45 in.), temperature (55–64° F.) 15 obs.
Group 2. Rainfall (32–38 in.), temperature (58–80° F.) 39 obs.
Group 3. Rainfall (23–38 in.), temperature (66–69° F.) 30 obs.

For groups 1 and 2 no significant relationship was found between soil organic matter and temperature. This indicates that, within the temperature ranges shown, temperature had little effect on soil organic matter. On the other hand under constant temperature (group 3) the effect of rainfall on organic matter was very significant (equation 9).

$$\% \text{ O.M.} = 0{\cdot}085 \text{ in. rain} - 0{\cdot}05 \ (t = 3{\cdot}22, \text{ for P} = 0{\cdot}01, \ t = 2{\cdot}75) \quad (9)$$

The similarity of equations (9) and (5), although no allowance was made for temperature in equation (5), and the absence of a relationship between soil organic matter and temperature, show that temperature has a relatively minor effect, compared with rainfall, on the organic-matter content of the soils. A similar observation has been reported by Prescott (1931) for Australian soils.

The Relationship between Clay Content and Organic Matter

No significant relationship was found for the surface profile samples between organic matter and clay contents. When, however, a group of fifteen soils low in clay (about 27 per cent.), at high altitudes, and under high rainfall and undisturbed forest vegetation, were eliminated the regression of organic matter on clay was very significant (equation (10)).

$$\% \text{ O.M.} = 0{\cdot}04\% \text{ clay} + 1{\cdot}23 \ (t = 5{\cdot}336, \text{ for P} = 0{\cdot}001, \ t = 3{\cdot}291) \quad (10)$$

It appears, however, that the relationship is not a direct one but an indirect one involving rainfall. In support of this it was found that the regression of clay content on rainfall was barely significant (P = 0·05) but when the same group of fifteen soils was eliminated the regression was very significant (equation (11)).

$$\% \text{ clay} = 0{\cdot}39 \text{ in. rain} + 24{\cdot}4 \ (t = 2{\cdot}85, \text{ for P} = 0{\cdot}01, \ t = 2{\cdot}576) \quad (11)$$

Since the organic-matter content is only significantly related to the clay content when the latter is significantly related to rainfall, it appears that the significance of equation (10) depends on the clay content functioning as a reflection of rainfall.

Equations (2) and (3) show, however, that under constant rainfall the clay content of the soil can influence the organic-matter content, so that the significance of equation (10) cannot be ascribed entirely to rainfall.

From the evidence available it appears, however, that clay content compared with rainfall is a minor factor in its influence on organic matter in soils. Outside certain limits, however, it can clearly become a major factor as shown by the low organic-matter contents, in spite of high rainfall, associated with the two sandy soils discussed earlier.

C:N Ratios

These were calculated from $\frac{\%C \text{ (uncorrected)} \times 1{\cdot}33}{\%N}$ and the average value for the surface profile samples was 13·1. No significant relationships were found between the C:N ratios and rainfall, organic-matter content or clay content. Hosking (1935) also found no general correlation of the C:N ratio with climatic conditions for Australian soils.

Discussion

The organic-matter status of the East African soils is relatively high, and compares favourably with that of temperate countries. This agrees with the results found for other tropical countries, particularly Costa Rica, Puerto Rico, and Colombia, and further illustrates that tropical soils are not, in general, deficient in organic matter. In this respect the high chroma of many tropical soils, particularly the red and yellow ones, can be misleading and was no doubt responsible for the earlier theories that tropical soils contain little or no organic matter. Milne (1937) and Vageler (1930) postulate that tropical humus substances are colourless, or nearly so. It may not, however, be necessary to postulate the presence of colourless humus substances to account for bright coloured soils with high organic-matter contents. The buffering capacity of such soils to colour change may be so high that considerable amounts of dark material are required sensibly to reduce their chroma. Thus, when a bright red soil here was mixed with black soil of equal fineness in the proportion of 5 to 1, its chroma was barely reduced from 10 R.4/8 to 10 R.4/6.

Rainfall appears to be the major factor governing the organic-matter and nitrogen contents of the East African soils. The similarity of the relationships between nitrogen and rainfall for East Africa and parts of North America, and between nitrogen and the humidity factor for Australia and North America suggests that temperature is a less important factor. Prescott (1931) in fact found no direct effect of temperature on the nitrogen content of Australian soils over a range of 56–77° F. Presumably the relationship between rainfall and organic-matter or nitrogen content of the soil is a relatively simple one in which increasing rainfall favours increasing vegetative growth and therefore production of organic matter without having much effect on its rate of decomposition. The influence of temperature on the other hand is more complicated in that increasing temperature, within limits, favours both the rate of production and decomposition of organic matter. The relationship, however, is not a simple one, and the diagram produced by Mohr (1930), showing how plant growth and aerobic and anaerobic decomposition depend on temperature, is of limited value since it takes no account of modifying

influences such as rainfall distribution. Thus in East Africa with its marked wet and dry seasons the effect of high temperatures on microbiological activity is nullified during part of the year by the adverse effect of dry conditions. This would slow down organic-matter decomposition in the surface soil without necessarily slowing down vegetative growth and organic-matter production provided moisture is available in the subsoil. Moreover, a rapid breakdown of plant residues does not preclude a build up in the soil of stable humus more resistant to microbiological activity. In view of such modifying influences it appears that too much emphasis has been placed, in the past, on temperature as a major factor in organic-matter decomposition in the tropics.

Jenny (1950) concludes that a large proportion of the soluble and dispersible decomposition products (humus) under high rainfall in Colombia migrate into the mineral soil, where the rate of decomposition appears to be slow as a result of which humus accumulates fairly rapidly to a high level. Recent work summarized by Broadbent (1953) and Ensminger and Pearson (1950) on the interaction of the soil organic fraction with clay minerals to form complexes indicates that such reactions can, *inter alia*, account for the slow rate of decomposition mentioned by Jenny. For example, unpublished data by Ensminger show that the addition of montmorillonitic clays to proteins and to Florida peat rendered them less susceptible to microbial decomposition under laboratory conditions; while Allison *et al.* (1949) found that the nature and amount of colloid present in sand-colloid mixtures in which organic materials were decomposing is an important factor in determining the quantity of residual carbon after a year of decomposition. Whatever the protective mechanism may be it is apparent that soil clay, depending on the amount and kind present, is a factor of some importance in conserving organic matter in tropical soils.

In the Kenya Highlands the organic-matter and nitrogen contents of the soils are relatively high (5·0–8·0 per cent. organic matter and 0·25–0·40 per cent. nitrogen) except for a particular area where the organic matter ranges from about 2·3 to 4·0 per cent. and the nitrogen from about 0·1 to 0·2 per cent. The lower values are associated with shallow soils where continuous wheat cultivation and burning of the crop residues in the field has been practised. Only these soils have shown a consistent and significant response to nitrogen in the Kenya Highlands. On this basis there appears to be a relationship between total nitrogen and available nitrogen similar to that described by Allison and Sterling (1949). Their work indicated that in a given soil type and under like climatic conditions thoroughly humified soil organic matter is fairly uniform in quality regardless of past agronomic treatment, and that the total nitrogen content under these conditions appears to be a rough index of the nitrate-furnishing powers of variously treated soils. Even though restricted to a particular climate and soil type this relationship between total and available nitrogen, if further confirmed, should prove most useful in soil fertility studies.

From the preceding paragraph and what has been said earlier it appears that the soils in the more temperate parts of East Africa are

not deficient in available nitrogen, except when the organic-matter status for one reason or another is low. The problem, therefore, is not so much one of building up the available nitrogen in the soil as of conserving that already present by determining the best cropping systems and management practices to maintain a desirable available nitrogen balance. Such practices should include adequate protection against erosion, a proper selection of crop and grass rotations (including legumes), and conservation of crop residues.

Summary

A study has been made of the organic-matter and total-nitrogen contents of soils distributed mainly throughout Kenya, East Africa. The samples were collected from sea-level to 10,000 ft. and covered a range of climatic conditions. Generally speaking the amounts of organic matter and nitrogen in the soils proved to be fairly high and compared very favourably with the amounts in temperate soils.

The main factor governing the organic-matter and nitrogen contents was found to be rainfall; temperature and the clay content of the soils proved to be minor factors, very sandy soils excepted. The regression of total nitrogen on rainfall was very similar to that reported for two areas in North America. It is considered that the direct effect of temperature on the organic-matter and nitrogen status of the soils is small compared with that of rainfall, because increasing rainfall works more wholly in favour of vegetative growth and organic-matter production than increasing temperature, the effect of which on increasing vegetative growth and organic-matter production is counterbalanced by increasing microbiological activity and organic-matter destruction, at least within the temperature range encountered in these studies.

It is concluded that in the more temperate agricultural areas in Kenya the available nitrogen status is generally satisfactory and that attempts should be made to conserve this by determining the best cropping systems and management practices.

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THE CASING LAYER IN THE CULTIVATION OF THE MUSHROOM (*PSALLIOTA HORTENSIS*)

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WRITING of soil for casing mushroom beds Robinson in 1870 states 'As regards the kind of soil used in earthing, it is not of nearly so much importance as is generally supposed; almost any soil will do; but those having heaps of good maiden loam laid by for gardening purposes will prefer to use a coating of that.'

Since then growers have found that this is not so; the type of soil, its physical and chemical properties and subsequent treatment exert a considerable influence on the number and weight of mushrooms produced. Until recently, knowledge of the best types of soil to use has been obtained by hard and sometimes costly experience.

It has not been found possible, so far, to induce sporophore (fruiting-body) production in pure culture. In order to obtain sporophores it is necessary to grow the mushroom in compost and to case with a layer of a material such as soil or peat. The necessity of using such materials of variable and complex composition makes the carrying out of controlled experiments difficult and great care is needed in the interpretation of results. The cultural management of the cropping experiments presents many problems. Because of the very nature of the growing media a controlled alteration in one property causes many unknown variations in related properties. Despite these difficulties sufficient use of statistical methods in experimental design and interpretation of results has not always been made. This together with a lack of detailed information of the experimental methods and procedures used in some instances has made it difficult to assess the true value of some of the results which have been reported.

The fact that the mushroom fruiting body cannot be obtained from pure culture has resulted in very little work being done on the biochemistry of the processes of sporophore formation and growth. The growth and development during the mycelial stage has been studied in some detail. With the development of chromatographic and related methods of analysis there are signs that our knowledge of the biochemistry of the fruiting stage may soon be widened. Without better knowledge of this aspect of the problem, it is impossible to obtain a complete understanding of the functions of the casing layer.

Under commercial conditions the mushroom mycelium permeating the compost cannot be induced to form sporophores in any quantity until a covering layer of casing material has been applied. A few exceptional instances of sporophores developing on compost without casing have been reliably reported. A casing layer is thus not absolutely essential, but it would seem that the conditions favourable to sporophore formation are much more readily attained by the presence of such a

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layer. Soil is the usual casing material, but a variety of materials including peat, vermiculite, ground and broken bricks, ashes, and sand have been used either alone or in mixtures.

Many fungi are stimulated to form spore-bearing organs at the onset of conditions unfavourable for vegetative growth; such conditions may be lack of nutrients or changes in temperature and humidity. A function of the casing layer may be to supply such a stimulus. However, it is frequently observed that mycelium grows into the soil and covers the surface with a dense mycelial mat without forming sporophores. In fact the mycelium grows extremely well in most good casing materials during the cropping period. Another stimulus to fruiting is the accumulation of a reserve of carbohydrate in the mycelium. It has frequently been observed that the sporophores of the mushroom occur in flushes. The period between first spawning the compost and first picking is about 6 to 8 weeks and between subsequent flushes about 10 days. The duration of each flush is about 3 days. This pattern of behaviour is compatible with the accumulation of food reserves prior to fruiting, but does not explain the necessity for a casing layer.

In view of the general observation that fruiting in fungi is often a result of unfavourable conditions for vegetative growth, it is not surprising that the physical properties of the casing layer have received a great share of attention. Such properties as water-holding capacity, water content, structure, and porosity have been examined for relationships to cropping results. Chemical properties, apart from calcium status and pH, have not been examined to such an extent. This is probably due to early failures to obtain any correlation between some of the more common soil constituents, such as potassium and phosphorus, and cropping behaviour.

The function of a casing material in commercial mushroom cultivation can be broadly defined as being to induce sporophore production in quantity. A complementary function is to allow the mycelium in the compost beneath to grow and develop. It is probable that some properties of a casing material desirable for producing sporophores may conflict with the properties allowing proper mycelial growth in the compost.

There are two problems to be solved. Firstly, a biological one of determining the processes leading up to the formation of a sporophore, in its early stages referred to as a pinhead, and its subsequent development. Secondly, the practical problem of obtaining the maximum weight of fruiting bodies per unit area of growing space. The production of a large number of pinheads often leads to the failure of many of them to develop mature sporophores, presumably due to the shortage of readily available nutrient to supply all the pinheads which have formed.

Nutrient Status and pH

Pizer and Leaver (1947) attempted to classify several soils in accordance with their physical and chemical properties and cropping potentialities. They found no relation between yields and the following soil properties—available phosphorus and potassium, structure and texture.

In one instance the addition of chalk to a soil of pH 5·4 did produce an increase in yield. Yield varied with depth in the profile, and position in the field. Soils physically alike cropped differently, and the factors which influenced the cropping capacity were not transferred from one soil to another when used in separate layers; it was necessary to mix the soils before the cropping properties of one soil affected another. When used in separate layers it was the upper layer of soil which determined the yielding capacity.

No other chemical properties of the soils except pH and available phosphorus and potassium contents were measured, and some of the differences in yields may well have been due to variations in calcium or magnesium content. Both of these elements have since been shown to exert an influence upon yield.

Pizer and Leaver suggested that cropping is influenced by substances in the soil that are not very mobile. It seemed that close contact with the air was needed to make these substances effective.

Pizer (1950) has suggested that substances promoting cropping may be found and that plant residues may have a pronounced effect. From air-washing experiments Stoller (1943 and 1952*a*) has postulated the presence of a volatile substance produced by the mycelium, which when it accumulates inhibits fructification and that contact with oxygen in the air and a slightly alkaline soil are necessary for its decomposition thus allowing fruiting to occur. Borzini (1949) also reports evidence for the existence of substances in the soil that promote fructification. However, no successful attempts to isolate any such substances have been reported, but this is an aspect which warrants further and more careful investigation.

The increase in yield found by Pizer and Leaver when a soil of pH 5·4 was limed has been mentioned. Chapuis and Courtieu (1950) conclude from an investigation of soil pH, available calcium organic nitrogen and texture that certain limits are required for good yields. In agreement with Pizer and Leaver no effects due to available phosphorus and potassium could be found. However, the results of Chapuis and Courtieu are open to some doubt. Variations in soil properties were obtained by mixing soils of different composition. Thus many other soil properties both physical and chemical were altered simultaneously.

There is general agreement about the optimum range of soil pH for maximum yield. Kleermaeker (1954) considers soil pH to be more important than the physical properties of the soil. Chapuis and Courtieu found pH 7·2 to 8·2 (method unstated) to be the best range. They also found that whatever the original soil pH, at the end of the cropping period the pH was between 7·0 and 8·5. Most of the other workers report a gradual decrease in pH during cropping. The question of soil pH and yield has been investigated in America by Lambert and Humfeld (1939). They obtained low pH values by the addition of sulphuric acid and high values by addition of calcium hydroxide. The pH range covered by their investigation was 4·4 to 8·7 and probably higher as the method of pH measurements used did not allow for measurements of pH values above 8·7 (quinhydrone method). The possibility that yields

obtained at low pH values were due to excess sulphate and not low pH was checked by using a naturally acid soil and observing the effect of additions of chalk. The pH range 5·5 to 8·0 was found to be quite suitable with an optimum at 7·6. Lambert and Humfeld also found that chalk added to the soil in large quantities (up to 25 per cent.) was not harmful.

Evidence that the use of calcium hydroxide (20 lb. per ton) producing a high initial pH (glass electrode) is harmful has also been found in this country (Edwards and Flegg, 1952) but calcium carbonate at 27 lb. per ton of soil (the equivalent of 20 lb. of calcium hydroxide) had no depressing effect upon yield.

The effects of several levels of calcium have also been investigated, no difference being found between applications of 7 and 14 lb. chalk per ton of soil and a mixture of 7 lb. chalk and 21 lb. gypsum per ton. The pH of the treated soils was very close, being between 7·2 and 7·6. However, beds cased with the same soil unlimed, although the pH was 7·5, did not yield as well as those cased with the soil limed with either calcium hydroxide or calcium carbonate. Unfortunately none of the soils were analysed for calcium content. Thus quite apart from its effect upon pH calcium appears to be beneficial. Treschow (1944) has shown in pure culture experiments that calcium is an indispensable nutrient for mycelial growth.

Soils of very high or very low pH are therefore unsuitable; a pH of about 7·5 appears to be the optimum. There is little danger of adding too much lime as carbonate; in fact mushrooms are produced satisfactorily when a chalk soil is used. There is a danger of producing a high pH in the soil if calcium hydroxide is used, but this can be overcome by allowing the treated soil to weather for some time.

There is evidence (Anon, 1949) that a high magnesium content in the soil has a depressing effect upon yield. The toxic effect of magnesium in pure culture has been demonstrated by Treschow (1944) and Gandy (1953). Magnesium added to synthetic composts was also found to reduce yields (Edwards, 1949). The effect of magnesium toxicity may be serious if magnesium limestones are used to adjust soil pH.

It is the practice of some growers to add various other substances to the soil either at casing or during cropping. Bels-Koning (1950) has concluded from the use of substances such as vermiculite, ground brick, cloth, and filter paper that no nutritive elements are required in the soil. It is by no means certain that these materials were in fact devoid of all nutrients. Even so, if no nutrients are necessary in the soil it does not mean that the presence of some may not prove beneficial. The addition of a variety of substances to the casing material has been tried experimentally by Stoller (1952*a*) and Edwards (1953), and although some appeared to increase the yield it is impossible to assess the value of additions to the casing without further and more careful experiments.

Water Relationships

After casing, the beds are watered at frequent intervals throughout the cropping period. The casing layer absorbs this water and releases

it to the atmosphere by evaporation. The layer of moist casing material serves to keep the compost surface moist much more readily than could be achieved by applying water directly to the compost. There is consequently a region of high humidity directly above the compost, in the casing pore-space and immediately above the casing layer.

The first attempt to investigate the influence of the water-holding properties of casing soils on yield was by Bels-Koning (1950). It was found that the better the water-holding capacity the higher the yield obtained, provided that the material used allowed sufficient aeration. This was thought to be because the materials of high water-holding capacity had a greater reserve of available water than those of low water-holding capacity. It was found that a mixture of peat and vermiculite produced better yields when kept wet (25 per cent. moisture) than when kept much drier (10 per cent.).

Interaction between moisture content of compost and soil was also investigated; a dry soil produced better than a wet soil on a wet compost and a wet soil better than a dry one on relatively dry compost. From this it would seem that there was transfer of water from wet to dry material and extremes of wetness and dryness tended to be evened out.

The effect of water-holding properties and amount of water in the soil have been further studied (Edwards and Flegg, 1952) in terms of soil moisture tension. A large number of 8-in. plastic plant pots allowed a considerable number of replicates. Two clay soils, one of poor structure and one fairly well aggregated, and a sandy soil with and without peat added were used. Rough moisture-tension curves were obtained for these soils by determination of maximum water-holding capacity and the moisture equivalent by a suction method (Flegg, 1951) and wilting-point by placing the soils in an atmosphere of R.H. 98 per cent. The moisture content of the casing layer and compost was determined from time to time and checked between determinations by weighing the pots.

The best yields were obtained when the soils were kept within the range pF 2·7 to 3·9. Where the moisture tension rose above pF 4·0 yields were practically nil. There is thus evidence that there is a point analogous to the plant wilting-point beyond which sporophore formation does not occur.

Using mixtures of peat and sand and peat and vermiculite it has been found that yields were sometimes higher when such mixtures were applied and kept practically saturated than at intermediate or lower moisture contents (Edwards, 1953; Bels-Koning, 1950).

There is no doubt that water relationships in the casing layer are of considerable importance. It is not yet clear, however, to what extent the casing layer acts as a reserve of available water upon which the developing sporophore can draw, or serves mainly to produce a high relative humidity from about 99 to 100 per cent. immediately above the compost.

Structure and Permeability

It has been observed many times that soil type exerts an influence on the type of sporophore produced; sandy soils often produce small light

mushrooms whereas on clay soils the sporophores are generally heavier and larger. Lambert and Humfeld (1933) investigated the effect of soil type on yield and found that clay soils gave earlier and better yields. These differences may be in part due to differences in water-holding capacity. When clay loam soils in poor physical condition were used, puddling and cracking occurred and yields were negligible. They attribute the better yields of the heavier soils to their greater reserve of available water. However, physical condition appears to play some part. Bels-Koning (1950) stresses that the rate of aeration of the compost allowed by the casing layer is important and that the particle or aggregate size of the material can affect this. Chapuis and Courtieu (1950) have reported that a fine soil causes anaerobic conditions in the compost and yield is reduced.

Edwards (1952) has found that a clay subsoil sieved to contain lumps $\frac{1}{4}$–$\frac{3}{4}$ in. yielded better than the same soil sieved to $\frac{1}{4}$ in. or a 1 : 1 mixture of these grades ($P > 0{\cdot}01$).

Using peat, sand, and vermiculite mixtures a significant relation ($P > 0{\cdot}05$) between free pore-space of the mixtures when air-dry and number of mushrooms has been obtained (Edwards and Flegg, 1953), the number of mushrooms being greater with increasing pore-space. A similar relationship between the free pore-space when wet and yield was not quite significant.

It seems probable that the poor results found with soils in poor physical condition in the work of Lambert and Humfeld and the fine soil of Edwards are due to low porosity and permeability. Many growers find that soils which form a surface pan after continual watering do not yield well.

Some of the factors affecting the structure and stability of soils under mushroom growing conditions have been described (Edwards and Flegg, 1952). More recently Flegg (1954) has described the effect of changes in structure and stability upon pore-space and changes in pore-space upon conditions in the compost and casing layer. Aggregate size and degree of settling by tapping, degree of aggregate disintegration by different rates of watering and the stabilizing effect of mushroom mycelium each have their effect upon soil porosity.

The use of soil conditioners to maintain a high porosity has not been very successful (Edwards, 1952).

Burrows (1949) and Flegg (1953*a*) have calculated the amount of carbon dioxide produced per square foot in a bed 6–7 in. deep to be approximately 170–120 ml. per hour. Using the data for the diffusion of gases through soils (Penman, 1940*a* and *b*; Bavel, 1952; and Flegg, 1953*b*) and measurements of carbon dioxide concentrations in compost under the soil before and after watering made by Stoller (1936) and Lambert (1933) it has been shown by Flegg (1953*a* and 1954) that the interchange necessary to allow the carbon dioxide produced to escape can be accounted for by gaseous diffusion. This does not exclude the possibility that there are other mechanisms, such as thermal convection. The concentration of carbon dioxide in the compost has been found to vary from 0·2 to 0·4 per cent. just before watering to 2·0–5·0 per cent.

after watering has reduced the soil air-space. A similar rise and fall will no doubt occur with any other gas or vapour formed in the compost. The same factors which influence the changes in carbon dioxide concentration will affect the rate at which oxygen can diffuse into the compost.

Although there appears to be a relationship between reduced porosity and consequently slow rate of gaseous interchange and low yields, there is no experimental evidence on the effect of varying oxygen and carbon dioxide concentrations on mycelial growth. Stoller (1952*a*) and Lambert (1933) have reported the adverse effects of high concentrations of carbon dioxide in the air above the beds upon the development of sporophores.

Associated with the production of carbon dioxide in the compost there is production of heat, estimated by Edwards and Burrows (1954) to be 500 to 1,000 cals. per sq. ft. per hour. The temperature of the beds does not progressively increase during cropping, therefore the heat produced must escape in some way. It is probable that much of the heat is used up in evaporating water from the compost, the water vapour produced being removed by diffusion through the casing layer.

From the conclusions about the accumulation and rates of diffusion of carbon dioxide it is to be expected that under some circumstances the depth of casing material and time of casing would influence yield. Lambert and Humfeld (1939) found no difference between soil 1 and 3 in. deep. This may have been because the soil was sufficiently porous and that any critical concentration of carbon dioxide was not reached. Details of the soil used were not given. These workers found that the optimum time for casing was about 3 weeks after spawning.

Edwards (1952) has shown that an early crop was better cased after 14 days and a late crop after 21 days. The optimum time is probably dependent upon the stage of development of the mycelium in the compost.

Artificial Casing Mixtures

Because of the presence of disease and absence in some localities of a suitable casing soil, there is a need for a casing material which is readily available and free from disease. Bewley and Harnett (1938) have reported that the admixture of sand or peat with soil resulted in increased yields and that such materials as granite chips, stones, and peat alone produced reasonable yields. Bels-Koning (1950) has used such materials as peat, vermiculite, ground brick, cloth, and filter paper. The satisfactory use of a non-fibrous peat has been reported by Stoller (1952*b*).

Edwards and Flegg (1954), while using mixtures of clay, sand, peat, and vermiculite in order to produce a wide range of physical properties, found that a fibrous sphagnum peat with either vermiculite or sand was comparable with a good casing soil. These and similar mixtures are now being used to some extent in practice.

There is not, so far, sufficient evidence to show why the casing layer is so important. Several functions which it performs have been studied to a greater or lesser extent but the relationship between these functions

and the mechanism of sporophore formation and development is not yet clear.

It is hoped that this review shows not only the extent of our knowledge of mushroom casing layer but also the extent of our ignorance.

Summary of Features of the Casing Medium studied

	In soils	*In peat mixtures*
Calcium	Probably beneficial	Not examined but probably beneficial
Magnesium	Toxic	Not examined but probably toxic
Nitrogen	Uncertain	Not examined
Phosphorus	No effect	Uncertain
Potassium	No effect	Uncertain
Pore space (Structure and stability)	High pore space probably beneficial	
Water-holding capacity	Good reserve of available water beneficial	
Optimum water status	Above wilting-point and below field capacity	Probably as near saturation as possible
Optimum pH	Between 7·0 and 8·5	

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OCCURRENCE OF AN ALUMINIUM-SEPIOLITE IN A SOIL HAVING UNUSUAL WATER RELATIONSHIPS

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WITH ONE PLATE

Introduction

DURING an investigation of soils and their land use in the Coonalpyn Downs area, South Australia (Blackburn *et al.*, 1953; Jackson and Litchfield, 1954), Mr. G. Blackburn* requested a laboratory determination of the 15 atmosphere water content on a soil near Tintinara. A detailed examination of the soil showed it to be unusual in two respects. Firstly, in relation to its clay content, the water content at 15 atmospheres was remarkably high (1·32 g. H_2O per g. clay) and secondly, the dominant clay mineral gave a diffraction pattern similar to that of sepiolite. As the alumina content (7 per cent.) of this mineral was higher than expected from sepiolite, it has been called aluminium-sepiolite.

Location and Description of Soil

The soil† is situated in a swamp of about 200 acres near Tintinara (Section 37/N[1] S. of Tintinara, South Australia) in an area of winter rainfall of about 18 in. per year. The profile is shallow; the upper 10 in. consists of black to grey clayey soil high in organic matter and soluble salts, and is underlain by 2 to 3 in. of grey clay, high in carbonates. Beneath this, marl extends to the water table which, at the time of sampling (November), was at a depth of 40 in. The soil profile contains a few hard calcareous nodules.

Experimental

Soil samples were taken to a depth of 40 in. but most of the investigations were carried out on clay separated from the soil at a depth of 7 in. (clay content 25 per cent.). The soil was treated with hydrogen peroxide to remove organic matter, dispersed with calgon, and the clay fraction (less than 2 microns) was separated by repeated decantations. The clay was washed with 0·1 N HCl to remove carbonates, leached with 1 N NH_4Cl, washed, and air-dried (henceforth referred to as the clay separate).

X-ray analysis

X-ray diffraction photographs were taken of untreated soils, clay fractions, and calcareous materials. In the clay from the surface soil (1–6 in.) Al-sepiolite, montmorillonite, illite, kaolin, and fine-grained dolomite were identified. At a depth of 7 in. the clay was a mixture of Al-sepiolite and fine-grained dolomite. After acid treatment this clay gave diffraction data in good agreement with that quoted by Caillère

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† C.S.I.R.O. Division of Soils reference no. 18189–93; classified as Solonchak.

(1951) for sepiolite and that given by the A.S.T.M. Crystallographic Index for pilolite. Table 1 gives X-ray diffraction data for Al-sepiolite (clay separate), sepiolite, pilolite, and palygorskite. Below 7 in. to the greatest depth sampled (40 in.) Al-sepiolite was the only clay mineral

TABLE 1

X-ray Diffraction Data for Al-Sepiolite, Sepiolite, Pilolite, and Palygorskite

Al-Sepiolite (1)		*Sepiolite* (2)		*Pilolite* (3)		*Palygorskite* (4)		*Palygorskite* (5)	
d kX	I/I_1	d kX	I/I_1	d kX	I/I_1	d kX	I/I_1	d kX	I/I_1
12·2	100	12·15	100	12	100				
						10·5	100	10·5	100
7·4	10	7·6	30	7·6	30				
						6·50	20	6·44	60
						5·41	30	5·42	50
5·02	20	5·05	20	5·03	20				
4·52	80	4·60	100	4·54	50	4·46	70	4·49	80
4·31	60			4·32	60				
						4·16	60	4·18	30
				4·03	20				
3·76	20	3·82	50	3·76	40				
						3·67	30	3·69	50
								3·50	30
3·34	20	3·40	20	3·29	30	3·24	90	3·23	100
3·16	20	3·22	50	3·19	40				
				3·05	30	3·11	5	3·03	10
				2·83	10				
				2·71	20				
2·58	70	2·61	80	2·58	80	2·61	20	2·61	80
						2·52	70	2·55	30
2·44	30	2·45	70	2·43	50				
				2·37	10			2·38	30
2·25	30	2·28	60	2·27	50	2·25	5		
				2·17	20	2·14	20B	2·15	50
2·06	10	2·09	50	2·12	10				
		1·97	10	1·96	10				
		1·88	20	1·88	20			1·82	10
		1·71	20	1·70	30	1·67	20		
		1·60	40	1·59	30	1·60	10	1·62	10
		1·56	40	1·55	20	1·55	20	1·56	30
1·51	60	1·52	20	1·52	40	1·50	30	1·50	30
				1·51	20				
				1·47	10	1·48	5		
		1·38	20	1·42	40				
		1·36	20	1·35	20				
1·30	20	1·31	30			1·30	30		

B = broad.

(1) Clay separate from Tintinara, S. Australia (see Table 2 (1) for chemical analysis).
(2) Caillère (1951).
(3) A.S.T.M. Crystallographic Index, Card No. 2–0034; mean of two patterns, one material from Chile and the other from Euboa, Greece.
(4) Mt. Flinders, Queensland, Australia (Rogers *et al.*, 1954) (see Table 2 (4) for chemical analysis).
(5) Caillère and Hénin (1951).

recognized. The calcareous material in the nodules found in the soil and in the underlying marl was dolomite which in some specimens was very fine grained. A little calcite may have been present. Quartz was present in all the untreated samples examined.

Chemical analysis

In Table 2 the results of a chemical analysis[1] carried out on the Al-sepiolite are given and are compared with published data for sepiolite, pilolite, and palygorskite. The exchange capacity of the clay using Ca^{++} was 45 m.e. per 100 g. of oven-dry clay.

TABLE 2

Chemical Analyses of Al-Sepiolite, Sepiolite, Pilolite, and Palygorskite

	Al-Sepiolite (1)	*Sepiolite* (2)	*Pilolite* (3)	*Palygorskite* (4)	*Palygorskite* (5)
SiO_2	52·43	54·83	51·428	54·34	55·03
Al_2O_3	7·05	0·28	7·515	6·29	10·24
TiO_2	..	..	..	0·91	..
Fe_2O_3	2·24	0·45	2·06	3·87	3·53
FeO	2·4	..	2·486		
MgO	15·08	24·51	9·35	12·98	10·49
CaO	..	0·55	0·581	(< 0·01)	..
MnO	trace	..	1·298	..	..
NH_3	0·58	..	..	..	..
K_2O	..	0·03	..	..	0·47
Na_2O	..	0·35	..	..	..
H_2O-	10·48	8·18	10·88	8·00	9·73
H_2O+	9·45	10·74	14·163	13·04	10·13
Total	99·71	99·92	99·761	99·43	99·62
Exchange capacity*	45	..	..	5·7	21

* Expressed in m.e. per 100 g.

(1) Clay separate, Tintinara, S. Australia.
(2) Yavapai County, Arizona, U.S.A. (Grim, 1953).
(3) Tod Head, Scotland (Heddle, 1879).
(4) Mt. Flinders, Queensland, Australia (after Rogers *et al.*, 1954).
(5) Attapulgis, Georgia (Grim, 1953).

Electron micrographs

Electron micrographs were taken by Dr. S. G. Tomlin[2] of the clay separate and of a palygorskite from Queensland (see Plate I). Although the average particle size of the clay separate is small (0·2 μ long $\times$ 0·02 μ diameter)—compared with the palygorskite (1 $\mu \times 0{\cdot}05$ μ)—its fibrous nature is apparent. Davis *et al.* (1950) have given a number of electron micrographs of sepiolite and palygorskite from several sources. The particle size of both these minerals varied greatly; that of sepiolite

[1] Analysis by Mr. R. E. Shapter, Division of Soils, C.S.I.R.O., Adelaide, South Australia.

[2] Physics Department, University of Adelaide, Adelaide, South Australia.

(Meerschaum) from Turkey and attapulgite (palygorskite) from Georgia (Davis *et al.* loc. cit., Plate 33) resembled most closely that of the clay separate.

Physical properties

Samples of soil and the clay separate were wet under a tension of 2 cm. of water, placed in a pressure membrane apparatus (Richards, 1941), and brought to equilibrium with an air pressure of 15 atmospheres* (pF 4·2: relative vapour pressure 0·988). The soil was found to contain 0·33 g. of water per gramme of oven-dry soil, although the clay content was only 25 per cent. The water retention expressed relative to clay would be 1·32 g. H_2O per gramme. The clay separate gave a value of 1·20 g. H_2O per gramme.

Discussion

Nomenclature

Chemical analysis of the clay separate gave a much higher alumina and a much lower magnesia content than would be expected from sepiolite (see Table 2). However, on the X-ray powder diffraction data alone, the mineral appears to be identical with sepiolite (see Table 1). Since the name sepiolite is associated with the hydrous magnesium silicate containing very little or no aluminium, it is suggested that this mineral, relatively rich in aluminium and isostructural with sepiolite, be called aluminium-sepiolite.

It was considered, at first, on comparison with the diffraction data given by the A.S.T.M. Crystallographic Index (see Table 1) and with chemical data (Heddle, 1879) that the mineral was pilolite. However, Stephen (1954) has shown that at least one of Heddle's pilolites is palygorskite and there are no data to suggest that this sample differs from his others. It seems, therefore, that some or all of the mineral samples analysed by Heddle are palygorskite. Unfortunately there is no chemical analysis or reference to publication given for the pilolites in the A.S.T.M. Index, but the samples were from localities different from those of Heddle. Since the type specimens of Heddle are palygorskite or palygorskite and other minerals, it seems that pilolite should be discontinued as a mineral name.

Until recently it was considered that palygorskite was the aluminium mineral isostructural with sepiolite. However, the two minerals give distinct X-ray powder diffraction patterns and the more recent work of Nagy and Bradley (1954) has shown that, although related, they are structurally distinct. This difference is emphasized by a comparison of the Al-sepiolite from Tintinara and the palygorskite from Queensland which are almost identical chemically but give very different diffraction data.

* Richards and Weaver (1943) have shown that the water content obtained at this pressure corresponds to the permanent wilting percentage of plants in non-saline soils.

Occurrence

X-ray analysis showed Al-sepiolite in the marl underlying the soil and suggests that the Al-sepiolite in the soil is residual. The marl appears to be a lacustrine deposit laid down in recent times. The area around Tintinara is, in common with much of the south-east of South Australia, poorly drained. Hossfeld (1950) studied areas adjacent to Tintinara and showed that, in Pleistocene times, sand dunes caused restricted drainage with the formation of lakes, lagoons, and swamps. Environmental conditions similar to those of the Tintinara district existed in Pleistocene times over a very large region now known as the south-east of South Australia, and similar conditions exist today over large areas in that region. Many of the earlier lacustrine deposits have been buried beneath wind-blown sands. It seems likely, therefore, that sediments similar to that at Tintinara might occur throughout the area. The occurrence of Al-sepiolite with dolomite of lacustrine origin is similar to many occurrences of palygorskite (Millot, 1952; Kerr and Kulp, 1949; Rogers *et al.*, 1954).

The relationship between illite and kaolin occurring in the surface soil and the underlying Al-sepiolite is not certain. It is probable that the illite and kaolin, which are the dominant clay minerals of surrounding soils overlying other parent materials, have been transported by wind and water to the Tintinara site.

Water retention

To illustrate the unusual water retention of the clay from Tintinara some results for other soils and clays are given in Table 3. The first column gives the samples and their location and, where soils are used, the Great Soil Group. Column 2 gives the dominant clay minerals in the clay (less than 2 microns) fractions of the samples. With the exception of the Krasnozem, the clay fractions consisted of at least 95 per cent. of the dominant mineral. The Krasnozem clay contained, in addition to meta-halloysite, goethite, and gibbsite. Column 4 gives the water retained by the sample at pF 4·2 and the next column gives this result calculated relative to 100 per cent. clay. The last column shows experimental values of the water retained by clay separates of the samples.

It is seen that, in general, illite and kaolin retain less water at pF 4·2 than the other minerals. The results in Table 3, and others obtained in this laboratory, show that for these two minerals the exchangeable cation makes little difference. Preliminary experiments indicate that water retention increases with decreasing particle size. Montmorillonites retain more water than illite or kaolin, and this is to be expected because of the intracrystalline water of montmorillonite. Na-saturated samples of this mineral retain approximately 10 per cent. more water than the Ca-saturated clay. It has been found that particle size has no influence on the results obtained with montmorillonite. This can be accounted for by the fact that the maximum possible surface of montmorillonite is available for water retention irrespective of particle size. The high figures obtained for the fibrous minerals, palygorskite and

TABLE 3

Water Content at pF *4·2 for a Number of Soils and Clays**

Sample	*Clay mineral*	*Clay content* % $< 2\mu$	*Water Retained at* pF 4·2		
			g. H_2O/*g. sample*	*g.* H_2O/*g. clay (calculated)*	*g.* H_2O/*g. clay (experimental)*
Solonchak, Tintinara, S. Australia	Al-sepiolite	25	0·33	1·32	1·20
Sepiolite†	sepiolite	..	0·90	..	..
Palygorskite, Queensland	palygorskite	..	..	..	0·89
Wyoming, Bentonite, U.S.A.	montmorillonite	..	0·50	..	..
Montmorillonite, Rock River, Wyoming, U.S.A.	montmorillonite				
	Ca-saturated	..	..	..	0·69
	Na-saturated	..	..	..	0·78
Montmorillonite, Yavapai County, Arizona, U.S.A.	montmorillonite				
	Ca-saturated	..	..	..	0·62
	Na-saturated	..	..	..	0·67
Hydromorphic Black Earth, Lismore, N.S. Wales	montmorillonite	64	0·38	0·59	0·52
Illite, Illinois, U.S.A.	illite				
	Ca-saturated	..	..	..	0·33
	Na-saturated	..	..	..	0·34
Solonetz, Willalooka, S. Australia	illite	50	0·22	0·44	0·43
Indianite, Indiana, U.S.A.	meta-halloysite	..	..	..	0·53
Krasnozem, Lismore, N.S. Wales	meta-halloysite	68	0·24	0·35	0·35
China Clay, England	kaolinite	..	..	..	0·37
Laterite, Rocky Gully, W. Australia	kaolinite	55	0·17	0·30	0·38

* Except for palygorskite and sepiolite, these results have been taken from unpublished data of Stirk and Norrish.

† Obtained by courtesy of Dr. P. S. Hossfeld from the Geology Museum, Adelaide University, Adelaide, South Australia.

sepiolite, are probably due to the open packing of their fibres (see Plate I) which results in the formation of highly porous aggregates. The porous nature and low apparent specific gravity of mineral sepiolites and palygorskites are well known. The exceptionally high water retention of the clay from Tintinara is probably due to its smaller particle size. Results obtained on this clay with different cations (Na, Ca, NH_4) showed no significant differences. That the high water retention by the fibrous minerals is not purely a particle size-surface area effect is evident from a comparison of surface areas. The Al-sepiolite and the palygorskite have surface areas of approximately 10^6 and 4×10^5 cm.^{2} per gramme of clay, respectively, as calculated from the electron micrographs. Montmorillonites have a surface area of $7{\cdot}6\times10^6$ cm.^{2} per gramme available to water (calculated from crystallographic data) while the areas of the illitic clay from Willalooka and the kaolinitic clay from Rocky Gully are respectively $1{\cdot}5\times10^6$ and 4×10^5 cm.^{2} per gramme as measured by nitrogen adsorption.

As part of their crystal structure sepiolite and palygorskite have channels which are large enough to accommodate water molecules (Bradley, 1940; Nagy and Bradley, 1954) but since 1 g. H_2O per gramme clay corresponds to approximately 2·3 c.c. H_2O per c.c. clay it seems

unlikely that the channels could account for the high water retention of these materials.

The agreement between the last two columns of Table 3 indicates that for most soils all the water retained at pF 4·2 is associated with the clay.

Summary

The clay from a swamp soil near Tintinara, South Australia, was found to contain a mineral (referred to as aluminium-sepiolite) resembling sepiolite in structure and palygorskite in chemical composition. The water retention of this mineral at pF 4·2 is compared with that of other clay minerals and the order of increasing retention is as follows: kaolin and illite, montmorillonite, palygorskite, sepiolite, and aluminium-sepiolite. The high water retention of palygorskite and sepiolite is ascribed to the type of packing associated with fibrous particles. The particularly high value for Al-sepiolite is considered to arise from the fineness of the fibres.

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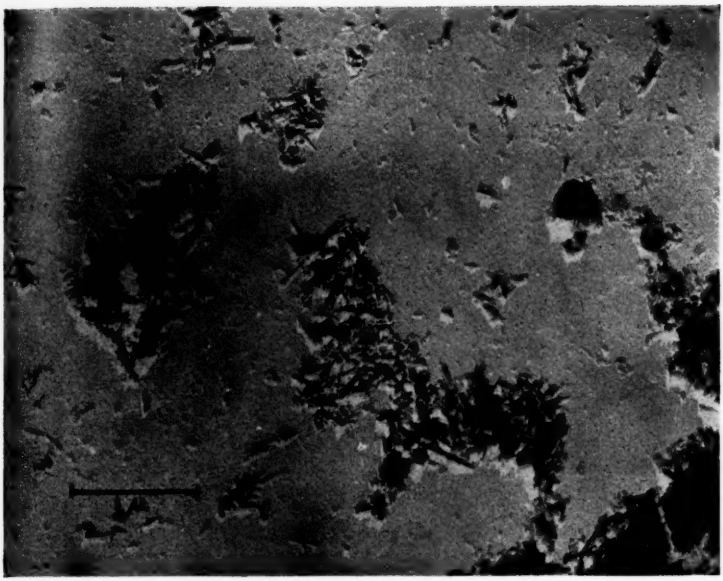

a. Clay separate (Al-sepiolite)

b. Palygorskite

Electron micrographs of clay separate from Tintinara, South Australia, and palygorskite from Mt. Flinders, Queensland

L. ROGERS, J. P. QUIRK, *and* K. NORRISH—PLATE I

PRELIMINARY NOTE ON CRISTOBALITE IN CLAY FRACTIONS OF VOLCANIC ASHES

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THE clay-mineral composition of Indonesian soils is being studied in the Institute for Soil Research at Bogor by means of the X-ray diffraction method. Moreover special attention is given to the variations of the clay-mineral associations in the various horizons of soil profiles, in connexion with the genesis of the soils.

The parent material of many Indonesian soils is volcanic ash. A knowledge of the primary minerals present in the clay fractions is therefore essential. X-ray photographs of clay fractions of recent volcanic ashes from active volcanoes on the island of Java were made. A preliminary study showed the presence of rather large amounts of α-cristobalite, especially in the finest clay fractions of all ashes investigated. Other minerals are present, but specific clay minerals were absent. This article is meant to show that α-cristobalite occurs primarily in the finest grades of volcanic ashes or tuff deposits.

The silica-mineral α-cristobalite, in the form of particles smaller than 2 microns, was mentioned for the first time by Hofmann and others (1934) in connexion with a bentonite from Rumania. This occurrence was thought to be an exception to the rule that the clay fraction only consisted of secondary minerals. Favejee (Hardon, 1939) found α-cristobalite in the clay fractions of a bleached soil from Bantam, Indonesia. The parent rock of this soil is a dacitic tuff. Favejee suggested that the α-cristobalite might be a characteristic mineral for bleached soils on dacitic tuff.

The occurrence of α-cristobalite in igneous rocks, however, has been previously recognized. Rogers (1928) writes that cristobalite is commonly found in cavities of volcanic rocks. It is a characteristic mineral, as spherulites, and is frequently associated with the silica modification tridymite. Microscopic investigation of lava rocks from San Juan (Colorado) by Larsen (1936) showed that cristobalite is the most common mineral in the gas cavities of basaltic lavas. In andesites and liparites it is less common, occurring mainly along the walls of the cavities of large spherulites, especially when these spherulites are embedded in obsidian. Cristobalite also occurs sometimes in submicroscopic intergrowths with feldspar in the ground mass of extrusive rocks (rhyolites, &c.) and in spherulites. This has been proved with X-ray studies by Hurlhut (1936).

Cristobalite has also been found in sedimentary rocks together with typical hydro-thermal minerals such as opal, montmorillonite, &c. Van der Marel (1950) cites from a paper of Gruner the occurrence of nearly 30 per cent. α-cristobalite in a thoroughly weathered volcanic-ash bed. Beljankin *et al.* (1938) mention the occurrence of substantial amounts of

cristobalite in an argillaceous quartz-sandstone, which is overlain by a basalt. They suggested that the cristobalite was directly formed from the quartz at a temperature of more than 870° C. as a consequence of the contact-effect of the basaltic lava.

The general conception of its genesis as put forward by Rogers, Larsen, and others, is that cristobalite in volcanic rocks is formed during the last stages of crystallization. In some cases it may be due to conversion at high temperature. In large cavities of volcanic rocks cristobalite is formed after crystallization of the ground mass in consequence of a supply of silica by steam and associated with multiple mineralizers. The genesis of cristobalite in dense parts of the ground mass, however, may occur according to Larsen (1936) by rapid or retarded crystallization, which is not 'lubricated' by mineralizers.

From the above-mentioned concepts of the genesis of cristobalite it is clear that this mineral can be expected in volcanic ashes. These ashes are formed by volcanic eruption and consist of disintegrated and pulverized material originating from rocks at the basement of the volcano, the diatrema and tuff material of the central part of the volcanic cone. These rocks have been subjected to contact-pneumatolitic and hydrothermal processes, which facilitate the formation of cristobalite.

Clay fractions of a number of volcanic ashes, collected from recent eruptions of the volcanoes Smeru, Kelut, and Merapi on the island of Java, have been analysed by X-rays. The ashes of the last two mentioned volcanoes consist of andesitic material, whereas those of Smeru, according to Baak (1949), are mixed with basaltic material derived from olivine-basalt rock at the basement of the young Smeru cone.

The clay fractions of the volcanic ashes investigated were obtained by separation according to the method of Mohr. For the technique of this mechanical analysis reference should be made to Mohr and van Baren (1954, p. 255). The size-frequency distributions of freshly fallen ashes of the same volcanoes have been described extensively by Baak (1949). The amounts of the finest fractions are very small. The average composition gives, according to Baak, for the fraction smaller than 0·5 micron less than 1 per cent. and for the fraction 5–2 micron less than 5 per cent.

X-ray analyses have been made mainly of the fraction less than 0·5 micron. From a few samples X-ray analyses were also made of the fractions 2–0·5 micron and 5–2 micron. All analyses were made with an X-ray tube with copper anode.

The X-ray diffraction patterns show that the $< 0{\cdot}5$-micron fractions of the volcanic ashes investigated contain large, but varying amounts of α-cristobalite. In some ash samples of Smeru, however, cristobalite sometimes occurs in a smaller quantity. Rather large (not to be estimated) amounts of amorphous volcanic glass are present next to the cristobalite. This is indicated by blackening of the film around the collimator opening. The determination of the amorphous material as glass has been deduced from the large amounts of volcanic glass in the silt and fine sand fractions of these volcanic ashes (Baak, 1949). Quartz is present in small amounts and a few still undetermined minerals some-

times occur in varying quantities. Typical clay minerals, as for example kaolinite, however, are absent.

The diffraction data of the < 0·5-micron, the 2–0·5-micron and the 5–2-micron fractions of the Smeru ash are given in Table 1.

TABLE 1

X-ray Data

< 0·5 *micron*		2–0·5 *micron*		5–2 *micron*		*Mineral*
d(Å)	I	d(Å)	I	d(Å)	I	..
4·45	w	4·45	w	..		crist.
4·06	vs	4·05	s	4·04	m	crist.
		3·75	f	3·78	w	..
		3·62	f	3·61	w	..
3·35	m	3·35	m	..		qu.
3·18	s	3·18	vs	3·18	vs	crist.
3·03	w	3·03	w	..		..
		2·92	w	2·92	w	..
2·87	w	2·83	w	2·83	w	crist.
		..		2·66	f	..
2·51	s	2·52	s	2·52	s	crist.
2·13	f	2·13	w	2·13	w	crist., qu.
		2·00	f	2·02	f	crist.
		1·92	f	1·93	f	crist.
		1·83	f	1·84	f	crist.
		1·77	f	1·77	f	crist.
		..		1·71	f	crist.
1·62	f	1·62	f	1·62	f	crist.
		1·54	f	..		crist.
1·49	f	1·48	w	1·49	w	crist.

crist. = cristobalite; qu. = quartz.
Scale of intensities (I): vs = very strong; s = strong; m = medium; w = weak; f = faint.

It may be mentioned that the presence of α-cristobalite has also been identified along with minerals of the clay-mineral group in a young ash soil, a few bleached soils, and high-mountain soils. The parent material of these soils consists of volcanic ash. So the α-cristobalite must be considered as a primary volcanic mineral.

For studies of soil genesis, therefore, it is important to know that α-cristobalite is a mineral of the parent rock and has not been formed during the soil-forming processes.

Furthermore, it should be remarked that the presence of cristobalite and quartz in the volcanic ashes investigated is of no importance for the plants from an agricultural point of view. Both minerals are very resistant to weathering. The occurrence of glasses of andesitic to basaltic origin in large quantity in the clay fractions, however, must be of great value. Intermediate or basic volcanic glass has a great susceptibility to weathering and can supply many chemical elements in a relatively short time.

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